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The nature, detection, and prevention of intergranular corrosion in 18 Cr-8 Ni stainless steel: stress-corrosion cracking in 18 Cr-8 Ni austenitic stainless steel ; 18 Cr-8 Ni stainless steel in high temperature service.

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Carnegie Institute of Technology

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THE NATURE, DETECTION, AND PREVENTION OF INTERGRANULAR CORROSION IN 18 Cr-8 Ni STAINLESS STEEL.

by

Arthur Horace Tuthill

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The purpose of this report is to present the facts and the theory concerning the nature, detection, and prevention of intergranular corrosion in ordinary and alloy modified 18 Cr- 8 Ni stainless steel, and to establish general principles to guide the engineer in selecting material for specific applications.

Among the materials of construction 18% chromium - 8% nickel stainless steel combines excellent mechanical properties with outstanding resistance to many corroding mediums to produce one of our most useful alloys. Unfortunately, the generally excellent corrosion resistance of this steel is marred by a susceptibility to intergranular, or intercrystalline, corrosion.

Metal in the vicinity of a weld may literally disintegrate in solutions which do not attack the remainder of the metal. New equipment or repaired equipment may fail in service while similar equipment under identical service conditions is giving long and satisfactory life. In the steel mill, sheets may become embrittled after a simple pickling operation.

It should be emphasized that such failures are rare. These occasional failures, however, pose a perplexing problem for the design engineer. He is charged with specifying the best and the least expensive material which will be uniformly reliable under service conditions.

Recognizing the problem, the metallurgist has set about solving it, but the solution has come only at an increase in cost. The design engineer, therefore, must be in a position to judge when the increase in cost to avoid the possibility of intergranular corrosion is justified.

Ordinary 18-8 is homogeneous austenite at high temperatures, but on slow cooling transforms to

ferrite and a carbide[9]. It is relatively easy, by rapid cooling, to maintain the homogeneous austenite untransformed down to room temperature. The austenite at room temperature is unstable, but can be maintained indefinitely untransformed. Cold work and an increase in temperature both tend to transform the unstable austenite into its more stable equilibrium components.

In order to better illustrate the foregoing, consider Figure (1), a pseudo-equilibrium diagram showin the approximate relationship of the phases in 18-8. The dotted lines represent considerable uncertainties.

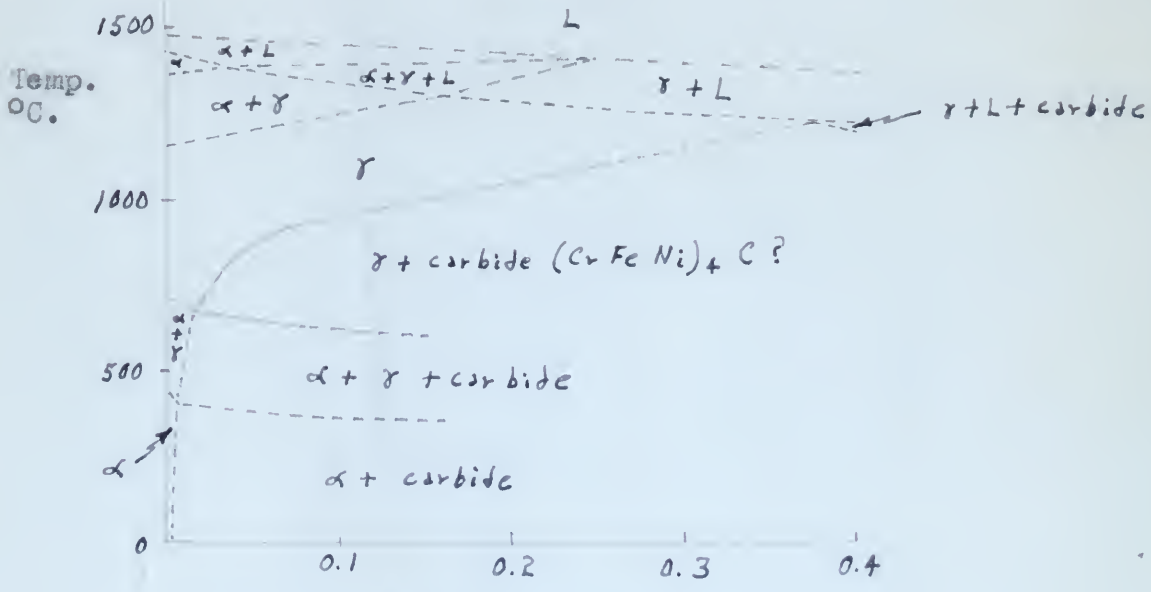

Figure (1). Effect of carbon on the constitution of alloys containing 18 per cent chromium and 8 per cent nickel, after Kinzel and Franks[9].

It is well to point out that Figure (1) is not a phase diagram, but a section through a quartenary diagram. Particular care should be used in applying it to 18-8 with alloy additions, for as Franks, Binder, and Bishop have shown, as little as 2% molybdenum introduces an entirely new phase, sigma[6]. No hint of this possibility is given in Figure (1). Uhlig has performed experiments which indicate that, in the absence of nitrogen, 18-8 itself is ferritic, not austenitic![27] With these limitations in mind, however, we shall find Figure (1) useful in picturing the transformations concerned with intergranular corrosion.

Figure (1) indicates several features. (1) Austenite (γ) is stable only at higher temperatures. (2) The solubility of carbon in austenite decreases markedly with decreasing temperature. (3) Ferrite, not austenite, is the stable or equilibrium phase below 400°C. (4) On slowly cooling an 18-8 sample containing 0.06% carbon, from the one phase (γ) region (1000°C.), we would expect a carbide to start precipitating rather rapidly at about 900°C. and ferrite to start forming at about 650°C.

Consider an 18-8 steel quenched from the one phase (γ) region and reheated to 400°C. A very finely divided precipitate begins to form at the grain boundaries at this temperature. As the temperature is increased the precipitate forms more rapidly, and near 650°C. it begins to coarsen. As we continue raising the temperature the

precipitate forms faster and becomes still coarser until in the vicinity of 900°C. it starts to redissolve. If the steel is not quenched from the austenitic region but is slowly cooled, the precipitate may form as it cools. The temperature range, 400°C. up to 850-900°C., is referred to as the "critical," "dangerous," or "sensitization" range.

While all the foregoing applies to 18 Cr- 8 Ni stainless steels, it is well to remember that other Cr-Ni and Cr-Mn austenitic stainless steels are also susceptible to intergranular corrosion.[9,10,15] In fact, some investigators have found similar conditions of grain boundary precipitate and intergranular corrosion in the ferritic chromium steels.[13,18] In general, however, the ferritic chromium steels are considered immune to intergranular corrosion. Whether they are, or not, is a point that might well bear further investigation.

The Nature of the Precipitate

Strauss observed the grain boundary precipitate and associated it with intergranular corrosion in the chromium-nickel steels as long ago as 1924.[24] Strauss, Bain, and others assumed that the precipitate was a chromium rich carbide, possibly Cr_4C.[1,15,16,25] Miller preferred to believe the precipitate was an iron carbide and that it gradually transformed to a chromium carbide as the temperature increased.[14]

Many investigators have noted that the carbide precipitation is sometimes, but not invariably, accompanied by ferrite formation.[1,9,11,15,16,29] The ferrite is easily detected for it is magnetic, whereas austenite is not.

The 400-900°C. temperature range of precipitation may be conveniently divided into two parts. From 400-650°C. the precipitate is so finely divided and so uniformly distributed along the grain boundaries as to be nearly continuous in nature.[1,2,13,14,28] It outlines the grain boundaries but is difficult to etch and detect even under the highest magnifications. In fact, Mathews suggests it may even be colloidal in size.[13]

Above 650°C. up to 900°C. where the precipitate starts redissolving, the precipitated particles become increasingly coarse and are easily distinguished as discrete, discontinuous particles. It is much easier to etch and is easily visible under low magnifications.[1,2,13,14,28] The coarser precipitate in the upper ranges does not render the material as susceptible to intergranular corrosion, the susceptibility apparently decreasing with increasing coarseness. The mechanical properties are slightly lowered, especially impact strength, as might be expected with a coarse grain boundary precipitate; however, though lowered, the Izod impact strength remains above 40 ft.-#.

Franks, as chairman of Subcommittee 6 on Metallography of A.S.T.M., is currently engaged in trying to determine the true identity of the grain boundary precipitate.[29] Both he and Miller have made X-ray analyses of residues from material sensitized at various temperatures, and have found Cr_4C only in the residues from the higher temperatures 750-850°C. [14,28] The residues from material sensitized in the lower temperature range were primarily austenite.

Some investigators feel that there may be two different precipitates, others that the finely divided precipitate formed at lower temperatures simply agglomerates. It makes little difference which viewpoint is adopted until there is more positive evidence as to the true identity of the precipitate. It should be noted, however, that 650°C. is not a sharp dividing point between two entirely different precipitates. It is the temperature at which Franks could detect the first evidence of coarsening,[20] and it is also about the temperature at which Bain and his co-workers found the maximum sensitization.[1]

The Theories of Intergranular Corrosion

The most generally accepted explanation of intergranular corrosion in austenitic stainless steels was proposed by Strauss, Schottky, and Hinnuber;[25] extended by Bain, Aborn, and Rutherford.[1] The theory

proposes that it is a chromium rich carbide precipitating at the grainboundaries. In precipitating, a carbon atom combines with the nearest four chromium atoms and forms Cr_4C (or some other chromium carbide), depleting the adjacent areas of chromium. With less than 12.5% Cr, corrosion proceeds in much the same manner as in a plain carbon steel. In some corroding mediums attack may be much more severe, and much more rapid than in a plain carbon or low Cr steel. The acceleration of the attack is often attributed to galvanic action between the precipitated particles and the matrix.[9] A vulnerable, and continuous, pathway of chromium-depleted material is opened up to any corroding medium.

The material will remain susceptible to intergranular attack until sufficient chromium has diffused from the center of the grains to build up the chromium content of the depleted areas. Since, presumably, carbon too must diffuse in order for precipitation to take place at all, it is necessary to assume that chromium is sluggish and diffuses at a very much slower rate than carbon, even at these relatively high temperatures.

Bain, Aborn, and Rutherford explain the recovery of sensitized material as chromium diffusion from the center of a grain to the depleted areas near the grain boundaries.[1] Their curve, Figure (2), for sensitization and recovery of a sample at 650°C. illustrates this point very well.

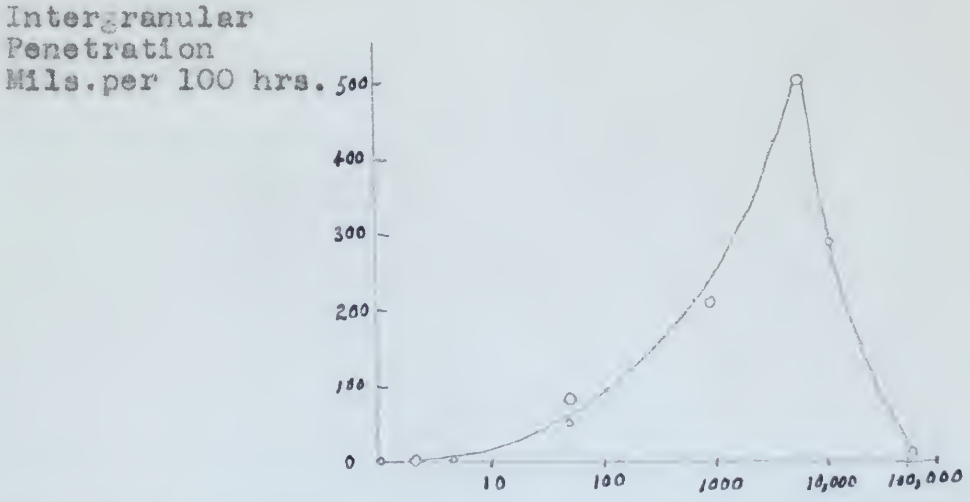

Figure (2). Sensitization and Restoration at 650°C. in 18-8 with 0.08% C, after Bain, Aborn, and Rutherford.[1]

Thus Figure (2) indicates that maximum sensitization is developed by holding at 650°C. for 8,000 minutes (5½ days). This implies that in only 5½ days the diffusion of chromium has been sufficient to start limiting the depleted area. 100,000 minutes (69⅓ days) are required, however, for the diffusion to build up the chromium content of all depleted areas and completely restore immunity to intergranular attack.

The chromium carbide theory obviously implies that the higher the carbon content, the greater the chromium depletion, and the greater the susceptibility

to intergranular attack. Bain and his co-workers found that the severity of intergranular attack increased directly with the carbon content.[1]

A more direct proof of the chromium carbide theory has been brought forward by DeSly and Haemers, and by Schafmeister.[4,22] Both analyzed the corroding medium after intergranular attack to determine the composition of the metal actually dissolved. Both found that the material dissolved in grain boundary attack contained only 9-10% chromium.

Before discussing the other theories of intergranular corrosion, certain other effects will be considered. Note that were the carbide to precipitate generally throughout the material, as is often the case in other steels, and not locally at the grain boundaries, we would not expect 18-8 to be susceptible to intergranular corrosion.

Grain size and cold work have important effects. The finer grained steels show considerable lag in developing grain boundary precipitates, a commercially important effect in 18-8 for welded construction.[1] Cold work prior to heating in the sensitization range tends to accelerate the precipitation at any temperature in the sensitization range, and drastically reduces the length of time at that temperature necessary to restore immunity.[1,7,9,11,12,14,15,19]

In attempting to explain intergranular corrosion, Kinzel has pointed out that the very fine,

uniformly divided precipitate at the grain boundaries introduces a second phase under the, theoretically, most favorable conditions for galvanic corrosion.[9] This is indeed so, but the precipitated second phase is still there after a long time heat treatment restoring immunity.

Miller suggests that it is Fe_3C which precipitates first in the finely divided state and that it is this finely divided Fe_3C precipitate which is attacked by the corroding medium.[14] Our knowledge of the reactivity of Fe_3C makes Miller's suggestion quite unattractive.

Miller, however, and also Mathews, directs attention to the fineness and continuity of the precipitate which seems to be primarily responsible for intergranular corrosion.[13,14] Mathews, particularly, points out that the precipitate, at least when first formed, is probably in the colloidal range. As the surface of a colloidal suspension is very large with respect to the amount of material, he considers this large surface important. It may well be that the surface effect is important, but in order to formulate a theory along those lines we must know more about the identity of the precipitate.

None of the theories other than the chromium carbide theory have suggested either a new or different attack, or solution to the problem. At least, until Subcommittee 6 completes its work on the identification

of the precipitate, the other theories can but serve to stimulate discussions.

Methods of Detecting Intergranular Corrosion

The most obvious method of testing for intergranular corrosion is to put a sample in a corroding medium and determine if it suffers grain boundary attack. Good data can be obtained with such a procedure in the laboratory, but it is not readily adaptable to field testing and inspection.

Investigators have almost universally adopted a boiling 10% H_2SO_4 - 10% $CuSO_4$ solution (some investigators prefer to vary the concentrations slightly) for the corroding medium. The H_2SO_4-$CuSO_4$ solution has been found to attack sensitized material along the grain boundaries in a reasonable time, but to have practically no effect on normal unsensitized material in the same grain.[1,2,4,9,10,12,15,16,25,30] This solution has often been referred to in the literature as the "Strauss" reagent, but Monypenny points out that the credit for developing it rightfully belongs to Dr. Hatfield of the Brown-Firth Research Laboratories.[15]

The methods of determining whether the H_2SO_4 - $CuSO_4$ solution has affected a sample consist primarily of measuring different physical properties that would be affected by intergranular corrosion. Rutherford and Aborn reasoned that grain boundary attack

meant opening small cracks between the grains, hence the electrical resistance should go up sharply. They found an accurate, sensitive, and quantitative relation between the electrical resistance and the severity of attack.[21] Considerable care is required in preparing the specimens, however.

Many investigators rely on the basic method of determining weight loss of a specimen after exposure to the boiling H_2SO_4-$CuSO_4$ solution. Reasonable sensitivity is attained though the electrical conductivity method is more easily interpreted for low orders of sensitivity. Microscopic examination of the surface layers exposed to the corroding medium will reveal intergranular cracks, if present. Careful examination should give as low order of sensitivity as the measurement of change in electrical conductivity and should be more easily interpreted than measurements of weight loss.

Payson subjects his samples to a "ring" test and a 180° bend.[16] Material that has suffered grain boundary attack loses its metallic ring. It will break or crack in the 180° bend test, provided the attack has progressed sufficiently. The "ring" test and 180° bend test are only qualitative, in that they will not measure how much attack has occurred, only indicate that it has occurred. The ability of the "ring" and bend test to indicate slight attack is questionable and certainly less reliable than measuring weight loss or electrical conductivity.

Microscopic examination alone can be relied upon to determine whether a given sample is in a sensitized condition or not, except in unusual cases. Samples which

have been exposed for varying periods at lower temperatures of sensitization, 400-650°C., may, or may not be sensitized depending on the period of exposure.[1,2,16,28] It is exceedingly difficult to etch the fine precipitate with Murakami's reagent, and but slightly less difficult to etch it with sodium cyanide.[2,16,28] Even though the etch may be successful, the fineness of the precipitate makes it difficult to resolve even at high magnifications.[1,2,28] Thus the absence of a precipitate may mean merely that we are unable to etch it or to see it. Payson seems to have had this difficulty, for he could find no precipitate in some samples severely attacked.[16]

The presence of a precipitate at the grain boundaries in 18-8 is excellent evidence that the sample is susceptible to intergranular attack. In isolated cases where the precipitate was formed and held for long periods in the 800-900°C. range, it is possible that enough chromium may have diffused to restore immunity. In such cases, testing in boiling H_2SO_4-$CuSO_4$ may be resorted to definitely establish susceptibility.

Many attempts have been made to associate sensitization with ferrite formation and ferrite's easily detectable magnetic properties. Payson and Krivobok have both conclusively proven, however, that ferrite can be present in material insensitive to grain boundary attack, and that other samples can be prepared

which suffer severe grain boundary attack but have no ferrite present.[11,16]

The recent development by Russell, Pray, and Miller of a non-destructive field test for susceptibility to intergranular corrosion in cast and wrought 18-8 is a welcome and useful addition to the older test methods.[20] The test is essentially an electropolishing operation using a lead cell and current from a storage battery. The solution contains 60% H_2SO_4 with 5 ml per liter of Glycyrrhiza extract. Two to two and one-half ml. of solution are required and the current is applied for three minutes. When susceptible, the grain boundaries are etched white and the difference between sensitized and unsensitized areas can be told by visual examination. The inventors claim a sensitivity corresponding to a 15% change in electrical resistance, which is indeed excellent sensitivity.

The older weight loss, electrical conductivity, and microscopic tests are primarily useful in the laboratory. The electropolishing test gives every promise of being a positive, rapid, and sensitive test that will find wide application in field testing equipment, particularly in the vicinity of welds.

Methods of Preventing Intergranular Corrosion

The chromium carbide theory assumes that the precipitation of chromium rich carbides at the grain boundaries depletes the adjacent areas of chromium and

thus opens up a vulnerable pathway for corrosion in the vicinity of the grain boundaries.[1,15] The obvious methods of preventing intergranular corrosion, then, are three: (1) maintain the carbon in solution by proper heat treatment; (2) reduce the amount of carbon available for combination with chromium to the point where no chromium carbide will precipitate; (3) control the chromium carbide precipitation in such a manner as not to leave a continuous, chromium-depleted network.

As was indicated in discussing Figure (1), a simple quench from high temperatures is sufficient to maintain austenite untransformed down to room temperature, i.e., keep the carbon in solution.

Welding, burning, riveting, high temperature service, and occasional unpredictable heatings in construction and repair involve holding the 18-8 in the sensitization range for varying lengths of time. Under such conditions, the carbides will precipitate, sensitizing the metal to intergranular attack. It should be emphasized that there are a great number of applications in which the possibility of reheating 18-8 to the sensitization range during service or repairs is negligible. When reheating is not a factor, it is but necessary to insure that 18-8 has been properly quenched, retaining the carbides in solution.

18-8 is quenched not only to keep the carbides in solution but also, and primarily, to produce

a homogeneous austenitic structure. The temperatures employed may be inferred from Figure (1). Kinzel and Franks state that homogenization in the 1000-1200°C. range followed by rapid cooling in water, oil, or even air retains the carbides in solution and produces fully softened, homogeneous austenite.[9] It is general practice to keep the finishing temperature for hot work above 900°C., preferably above 1000°C.,[9] and it is mandatory to quench to the fully softened structure with carbides in solution before pickling.

An increase in the temperature from which quenched improves the ductility, lowers the tensile strength, and increases the grain size.[9] Bain, Aborn and Rutherford have shown that an increase in grain size markedly increases the severity of intergranular attack particularly for short periods of time in the sensitization range.[1] Quenching temperatures higher than 1200°C. are to be avoided and, in general, the lowest temperature in the 1000-1200°C. range which gives complete homogenization in a reasonable time is to be preferred.

If it is feasible to follow any reheating operation such as welding with an anneal of the full section, the carbides precipitated during the welding operation may be redissolved and once more retained in homogeneous austenite upon quenching to room temperature.

A note of caution should be added at this point. Quenching does not produce uniform cooling throughout a section. The interior cools much slower than the surface. The thicker the section, the greater is the difference in surface and interior cooling rates. Thus with sections of some thickness it is quite probable that no possible quenching operation will cool the center portion fast enough to prevent precipitation of the carbides. Ordinarily it is the outside surface which is expected to resist corrosion, but the possibility of drilling, tapping, punching, and machining operations exposing interior, sensitized metal to the corroding medium cannot be overlooked.

If there is a distinct probability of heating 18-8 to temperatures in the sensitizing range during service or repair, and such heating cannot be followed by an annealing treatment, intergranular corrosion can still be prevented by reducing the effective carbon content to a point where no chromium carbides will precipitate on cooling.

It is possible to produce an 18-8 steel with less than 0.02% carbon (the solubility limit[1,14]), and such a steel is not susceptible to intergranular corrosion, even when heated for long periods in the sensitizing range.[2] Becket and Franks found very low carbon 18-8 to be noticeably magnetic, however, indicating that it was no longer homogeneous austenite. The difficulties encountered in producing an 18-8 steel with less than

0.02% carbon increase the cost sharply. Rather than reduce the carbon content all the way down to 0.02%, it becomes more economical to add an alloying element which is a stronger carbide former than chromium, thus effectively accomplishing the same result.[1]

Either titanium or columbium as alloy additions are eminently successful in preventing intergranular corrosion in 18-8.[1,2,7,9,11,13,15] The carbon content is held to as low a value as practical, 0.06% to 0.10%, in order to reduce the amount of alloy addition.[1,2,9] The amount of titanium required is 6 times the carbon content in excess of 0.02%, whereas the amount of columbium required is 10 times the total carbon content.[1,2,9] Titanium and columbium both are stronger carbide formers than chromium, and both, therefore, form a more stable carbide.

The function of the carbide forming alloy additions in preventing intergranular corrosion is to prevent chromium depletion by replacing chromium in the chromium rich carbides. Of necessity, the alloy additions must be given an opportunity to replace the chromium in order to be effective. This is accomplished by a "stabilizing" heat treatment at 850-900°C. for 2 to 4 hours. At these temperatures, even though the chromium carbide forms first, diffusion of titanium or columbium is sufficient to rapidly displace the chromium from the carbide.[1,2,7,11,13,15]

It is well to remember that if a titanium stabilized alloy is subsequently heated above 900°C., as in welding, part of the stable titanium carbide goes into solution and on cooling some chromium carbide precipitates, producing slight sensitization.[1] Even the slight sensitization thus produced is often noticeable in titanium stabilized 18-8 welded plate. Columbium carbide does not appear to dissolve in the area of the weld to the extent necessary to produce subsequent sensitization on cooling. Columbium stabilized 18-8 has a slight advantage over the titanium stabilized alloy in welded construction.

In the process of welding, molten metal from the rod is deposited on the cooler plates to be joined. There is a high loss of titanium through oxidation if titanium stabilized rod is used. Columbium stabilized rod gives very satisfactory results, and is universally preferred.[2,9,11] Titanium stabilized plate can be successfully welded with columbium stabilized rod, but the slight sensitization resulting from partial solution of the titanium carbide in the heated area near the weld may be objectionable. Columbium, too, has its disadvantages; for over 1% columbium decreases the ductility and toughness, but this is not a serious limitation provided carbon is held below 0.10%.[9]

Other alloy additions have been suggested, such as tantalum, vanadium, zirconium, and uranium to

perform the same function as titanium and columbium, but large amounts are required and no serious attempts have been made to develop such additions for general use.[1,9]

It is interesting to note that molybdenum, while markedly increasing the resistance of 18-8 to corrosion and particularly to pitting, reduces but does not eliminate intergranular corrosion. According to Franks, Binder, and Bishop, columbium in the amount of 10 times the carbon content is required, as in ordinary 18-8, to provide immunity in the molybdenum alloy.[6] Such an 18-8 alloy with both Mo and Cb has a wide range of applications under the severest corrosion conditions, but would be quite expensive.[6,9,10]

It is possible to make the excess carbide in 18-8 precipitate in such a manner as not to leave a continuous chromium depleted pathway for corrosion. Many investigators have shown the ordinary 18-8 can be immunized against intergranular corrosion by cold working fully annealed stock 50 to 75% and reheating in the 750-850°C. range for a few hours.[1,7,9,11,12,14,15,19] Cold working 18-8 introduces a great number of slip planes where the carbide can and will precipitate, thus producing a general precipitation and reducing the amount of carbide precipitation at the grain boundaries. When heated to the higher temperatures where appreciable chromium diffusion occurs, the time for recovery is

drastically reduced since much less grain boundary, chromium-depletion has occurred.[1,19]

It is also possible to introduce a small amount of ferrite and have the carbides precipitate in the ferrite primarily, instead of at the grain boundaries.[1,8,9,16,17,23,29] Payson took excellent photomicrographs showing the concentration of carbide precipitates in the ferrite.[16]

The presence of stable ferrite along with austenite may be induced by alloy additions,[16] increasing the chromium content,[1,8,16,23,29] and, according to Uhlig, by control of the nitrogen content.[27] Payson lists the following elements in varying amounts as promoting the tendency for stable ferrite, tungsten, molybdenum, vanadium, silicon, chromium (in amounts greater than 18%), and titanium.[16] He attributed the prevention of intergranular corrosion in titanium stabilized 18-8 in part, at least, to its stable ferrite forming tendencies.

Molybdenum was first added to 18-8 to reduce intergranular corrosion through the formation of small amounts of ferrite. It was found so effective in reducing pitting and general corrosion that the present tendency is to keep molybdenum around 2%, increase the nickel content, and prevent the formation of ferrite, thus restricting the effect of molybdenum to decreasing pitting and improving general corrosion resistance.

Then if resistance to intergranular corrosion is required, a columbium addition can be made.[6,10]

Payson and Krivobok both attempted to induce small amounts of ferrite with the hope that the carbides precipitating primarily in the ferrite would not precipitate at the grain boundaries in sufficient quantities to deplete the chromium content on short time heating and cooling cycles as in welding.[11,16] Neither Payson's alloy additions nor Krivibok's variations of the Cr-Ni ratio to produce small amounts of ferrite led to a sound solution, but they did lay the groundwork for the development of an interesting alloy developed by Scherer.[23]

Scherer investigated the effect of increasing the chromium content of 18-8. He found, as Payson had, that with 22-23% chromium, instead of homogeneous austenite there was 10-20% ferrite present.[23] He also found, as Payson, Krivobok, and other investigators had not, that on heating at 600°C. for a few hours longer than necessary to produce sensitization, the high chromium alloy recovered its immunity to intergranular corrosion.

Furthermore, many reheats above 900°C. and subsequent cooling did not reestablish a sensitized condition as would be expected. Scherer's results were confirmed and amplified by Hougardy, and Tofaute and Schottky.[8,26] It is interesting to note that Tofaute and Schottky replaced a portion of the nickel content with

nitrogen as several other investigators have done.[5,18,26] The primary objection to the high chromium and other 18-8 alloy modifications with 10-20% stable ferrite is a decided tendency to hot shortness.[29]

The high chromium, partially ferritic, stainless alloy developed by Scherer has possible application in welded construction where the presence of 15% ferrite does not produce undesirable mechanical properties, and where the ferrite does not lower the corrosion resistant to the environment to be met in service. In general, however, titanium and columbium stabilized alloys are to be preferred unless, as seems unlikely, there develops a considerable price differential in favor of the high chromium steel.

Conclusions

1. 18 Cr- 8 Ni austenitic stainless steel when cooled too slowly or when reheated to temperatures between 400°C. and 850°C.-900°C. usually precipitates a carbide at the grain boundaries and becomes susceptible to intergranular corrosion.

2. The heat treatment to give the desired structure for mechanical properties also retains the carbon in solution. Commercial practice is to heat and hold at 1000-1200°C. for homogenization, then quench in water, oil, or even air. Such heat treatment retains

the carbon in solution and produces a homogeneous, fully softened, austenitic structure.

3. It is generally believed that it is a chromium rich carbide which precipitates at the grain boundaries depleting the adjacent areas of chromium to the point where those areas will corrode much as ordinary steel. The very fine, slowly forming precipitate characteristic of the lower temperature range, 400-650°C., is associated with the severest intergranular attack. As the temperature of precipitation increases above 650°C. to 850-900°C. the precipitate forms faster and is coarser, but the severity of intergranular attack decreases, probably through the more rapid diffusion of chromium to the depleted areas. At temperatures from 850°C. upwards, depending upon the carbon content, there is an increasing tendency for the precipitated carbides to redissolve.

4. Boiling H_2SO_4-$CuSO_4$ solution is the corroding medium used to test for susceptibility to intergranular corrosion in the laboratory. The severity of intergranular attack may best be measured by weight loss or change in electrical resistance.

5. The electropolish test developed by Russell, Pray and Miller provides the engineer with a useful field test for susceptibility to intergranular corrosion.

6. Columbium or titanium stabilized 18-8

costing, respectively, 25% and 14% more than the ordinary 18-8* provide the only sure remedy for intergranular corrosion under all service conditions. The columbium or titanium replaces chromium in the carbide which forms. In small quantities, neither have any marked effect upon the mechanical or corrosion resistant properties of 18-8 other than the prevention of intergranular corrosion.

7. The choice between a titanium stabilized 18-8, currently quoted at 41 cents per pound and the columbium alloy, quoted at 45 cents per pound, may be largely determined on cost alone, except in welded construction. Columbium stabilized welding rods are universally preferred. In welded plate the columbium stabilized alloy has a slight advantage over the titanium stabilized alloy; for the columbium carbides do not seem to dissolve in the heated section near the weld to the extent necessary to allow chromium carbide precipitation and slight sensitization on cooling. Representative test welds can be made for a specific application to determine whether the higher-priced columbium stabilized alloy is required.

8. 18-8 alloyed with 2% molybdenum to increase the resistance to pitting and general corrosion, and stabilized with columbium to prevent intergranular corrosion provides the engineer with an excellent material for the severest service conditions, if cost can be a secondary consideration.

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*Costs are taken from current price lists.

9. In choosing 18-8 for a specific application, the design engineer should remember that intergranular corrosion is the exception, not the rule, and that it is difficult to interpret laboratory data in the terms of actual service conditions. He should consider the corroding medium and the range of temperatures likely to be met, as indicated hereinafter.

A. The corroding medium does not attack sensitized 18-8.

(1) Ordinary 18-8 is satisfactory within the limitations of its mechanical properties regardless of prior or subsequent heatings within the 400-900°C. sensitization range.

B. The corroding medium attacks sensitized 18-8.

(1) Service conditions which involve the possibility of heating within the 400-900°C. sensitization range do not, of course, justify the selection of the more expensive titanium and columbium stabilized alloys.

(2) Service conditions which involve the possibility of heating within the 400-900°C. range, but where the whole unit may be subsequently given a proper anneal, can also be met by ordinary 18-8.

(3) Service conditions which involve the possibility of heating within the 400-900°C.

range, as in welded assembly or repair, require the engineer to accept the increased cost of the titanium or columbium stabilized alloy in order to get the full benefit of 18-8.

10. The special 18-8 alloys with small percentages of ferrite present do not seem practical, for the homogeneity of fully austenitic 18-8 contributes in a large measure to its desirability.

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Stress - Corrosion Cracking in 18 Cr - 8 Ni Austenitic Stainless Steel

by

Arthur H. Tuthill

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It is the purpose of this report to present a comprehensive appraisal of stress corrosion cracking in 18 Cr - 8 Ni stainless steel at ordinary temperatures (room temperature to 200-300°C.). Intergranular corrosion in 18-8 has been extensively dealt with in the first report of this series. A familiarity with the theory and the extent of the susceptibility of 18-8 to grain boundary attack has been assumed, therefore, when discussing intergranular corrosion as it affects stress corrosion cracking.

Stress corrosion cracking of 18-8 is defined as a localized, grain boundary or transgranular cracking under the combined influence of a residual, or externally applied, stress and a corrosive environment.[16] The stress may be steady or it may vary, but it does not fluctuate with the frequency associated with fatigue stresses. It should be emphasized that a stress corrosion failure is local and that the metal adjacent to a crack, or between successive cracks is relatively unaffected and retains its ductility and strength.[1,6,13] Embrittlement of 18-8 by mercury and its salts, by zinc and bronze, and by various low melting or molten metals will not be considered as true stress corrosion in accordance with the suggestion of Mears, Brown, and Dix.[11,16]

The phenomenon of stress corrosion has long been recognized. Roberts-Austen in 1886 described what we now call stress corrosion cracking in reporting the embrittling effect of a ferric chloride solution upon a hard drawn bar of 13 carat gold (54.2 Au, 33.3 Cu, 12.5 Ag).[19] The season cracking of brass, and the caustic embrittlement of mild steel boiler plate have long been known and studied by the metallurgist.[7,16] In the development of the lighter aluminum and magnesium alloys, stress corrosion was a prominent factor. Mears, Brown, and Dix list a total of 26 alloys known to be susceptible to stress corrosion cracking under certain conditions.[16]

Seemingly inexplicable failures of 18-8 products under mildly corrosive conditions have been reported. In the oil industry 18-8 heat exchanger and condenser tubing has failed suddenly with a brittle fracture, while other 18-8 tubing in the same service went unaffected.[1,6] One such failure occurred in a cracked naphtha-water, 18-8 heat exchanger with highest temperature, 120°F.[6] Other similar failures in 18-8 autoclave linings have been reported from time to time.[6,12,21] Various other sudden brittle failures of 18-8 equipment such as coffee pots and hospital deep drawn pans are also recorded in the literature.[8,17] Most of these formerly inexplicable failures have been definitely identified as stress corrosion failures.

Fortunately such failures are rare, but they have tended to raise understandable misgivings about the use of 18-8 in certain applications, particularly in the oil industry. Dixon, in 1935, pointed out that the makers of 18-8 were losing a large potential 18-8 market to other alloy steels by their failure to study and find a remedy for the sudden brittle failures that plagued the users of 18-8 in the petroleum industry.[6] On the other hand, in 1944, Ellis, after seven years with the Research Laboratories of the American Rolling Mill Company had experienced only six cases of stress corrosion in 18-8 products and still considered stress corrosion failures as mere laboratory curiosities.[8] It is evident that stress corrosion is not a problem in most applications of 18-8, but that under certain combinations of service conditions it can become an important factor in influencing the design of units and the selection of material.

The Nature of Stress Corrosion

In considering the failure of 18-8 by stress corrosion, it is necessary to evaluate the possibility and the effects of the more common intergranular corrosion due to carbide precipitation and chromium depletion. Stress corrosion can and does occur in 18-8 which is susceptible to intergranular corrosion. It also occurs in 18-8 which has been stabilized by heat treatment or by

columbium or titanium additions and is immune to intergranular corrosion.[6,9,10,12,14,15,18,24,25]

18-8 stabilized either by heat treatment or by alloy additions was found susceptible to stress corrosion cracking in the presence of moist ethyl chloride.[14] Scheil describes the stress corrosion failure of a columbium stabilized stainless steel high pressure autoclave.[24] Franks, Binder, and Brown have determined that boiling solutions of lithium, amonium, magnesium, zinc, and calcium chloride will cause stress cracking in stabilized 18-8.[10]

Stress corrosion cracks in stabilized 18-8 are invariably transgranular.[10,14,24] Laboratory tests and service failures, however, give no clear cut picture as to the corrosive media that will cause stress corrosion cracking in stabilized 18-8. Nearly all investigators have used chloride solutions in attempting to induce cracking in stressed samples. Many chloride solutions, though, will not induce stress cracking in stabilized 18-8.[9,12] Some investigators have even reported stabilized 18-8 as immune to stress cracking because it did not stress crack in the particular corrosive medium they used.[3,10,13]

Ellis and Dixon, however, both report failures of stabilized 18-8 in mildly corrosive media such as naphtha and air, where there is no apparent reason to suspect the presence of the chloride ion.[1,6,8] Scheil does not specify the corrosive medium in a columbium stabilized

18-8 autoclave that failed.[21] From the difficulty investigators have experienced in finding solutions that will stress crack stabilized 18-8 it would appear that an investigation to determine whether the chloride ion is the sole offender might be fruitful.

The evidence in regard to stress corrosion of 18-8 which is susceptible to intergranular corrosion is more voluminous and more varied. Hodge and Miller found that as mild a corroding medium as boiler water and steam had caused stress corrosion failure of 18-8 susceptible to grain boundary attack.[12] Other corrosive media that will cause stress corrosion failures in 18-8 susceptible to grain boundary attack have been reported as ferric chloride (as low as 0.05%), mercuric chloride, nitric-hydrofluric acid solution, sulfuric acid - copper sulphate solution, sodium chloride - hydrogen peroxide solution, engine exhaust gases, and even air.[8,9,10,12,13,16]

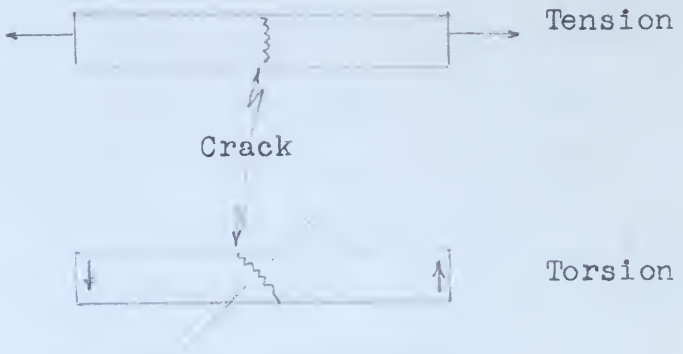
Stress corrosion failures in 18-8 susceptible to intergranular corrosion are primarily intercrystalline, but some cracks cross grains at times. Failures are more difficult to identify, for often the corrosive medium produces a general intercrystalline attack which tends to obscure a purely local stress corrosion crack or failure.[9,13,16,21]

It appears logical to assume that any corrosive medium which can cause intergranular attack may also cause stress corrosion cracking in sensitized 18-8.

It is not too important, however, whether 18-8 fails by intergranular attack or stress cracking, since it fails in either event. What might be helpful is an investigation to determine what corrosive media are too mild to attack sensitized 18-8 intergranularly, but will still cause stress corrosion failures. Boiler water, steam, and air apparently fall in this category.[8,12]

The Stress Characteristics

All investigators agree that the stress to cause stress corrosion cracking must be tensile, as logic suggests. None has observed stress corrosion induced by compressive stresses. Mears, Brown and Dix report an interesting experiment with an Al-Mg alloy.[16] One Al-Mg test bar was stressed in tension and a second was stressed in torsion. Both were subjected to the same corroding medium and cracked as shown.



It is significant to note that the second bar failed along the 45° plane across which the tensile force is greatest when the bar is stressed in torsion. The first bar with a pure tensile load failed transversely as indicated. Failure occurred in both bars in the plane, across which the greatest tensile force was acting, in preference to any other plane.

Investigators recognize that internal and externally applied stresses can initiate stress corrosion cracking. Sufficient internal stress to initiate stress corrosion can be produced by cold rolling, bending, and straightening, by grinding or welding, and by quenching to keep carbides in solution.[9,12,14,21]

It is particularly pertinent to realize that quenching 18-8 from 1000-1100°C. to retain the carbides in solution and prevent grain boundary attack, may produce internal stresses high enough to initiate stress corrosion in the proper corroding medium. Wilcox and Kosting have both found surface cracks in large 18-8 castings quenched from 1050-1120°C. These surface cracks could be stress corrosion cracks or quench cracks, but in either event they serve to emphasize the relatively high internal stresses that can result from quenching.[15] Benson has recently pointed out the serious magnitude of the internal stresses set up on quenching a low alloy steel from the temperature at which it was tempered. Tempering at 650°C. or higher

gives essentially complete stress relief. The samples quenched from this range and found to contain internal stresses serve to re-emphasize the fact that internal stresses are set up in quenching even though there be no phase change.

The quantitative results on the magnitude of the stress required to initiate stress corrosion cracking are sparse and difficult to correlate and interpret. Hodge and Miller reported that a threshold stress of 10,000 psi externally applied to an 18-8 test specimen sensitized to grain boundary attack was sufficient to initiate intergranular stress corrosion cracking in ferric chloride solutions.[12] Scheil reports that an internal residual stress of about 10,000 psi is sufficient to initiate stress corrosion cracking in 18-8 Cb and 18-8 Mo alloys when exposed to $MgCl_2$ solution.[21]

Franks, Binder, and Brown report that an externally applied stress slightly in excess of the yield strength at 0.2% offset is required to initiate stress corrosion cracking in 17 Cr-7 Ni and 18 Cr-8 Ni stainless steel stabilized by heat treatment against intergranular attack.[9] They used $MgCl_2$ as the corroding medium and their results supplement those of Scheil. Monypenny reports that his laboratories have obtained indications that 18-8 cold rolled to 200,000 psi tensile strength might stress crack in a 5-6% H Cl solution at room temperature in 24 hours.[17] When 18-8 was cold rolled to

180,000 psi tensile strength, stress cracking did not occur even if the sample were extenally stressed also.

Investigators have determined their data under different conditions which are not directly comparable. The data available indicate that externally applied tensile stresses in the neighborhood of the yield point are required to initiate stress corrosion cracking in stabilized 18-8, whereas residual, internal, tensile stresses may be much lower, about 10,000 psi, and still initiate cracking.

The experiment on the stress cracking of the Al-Mg bar in torsion showing that stress corrosion failure occurred across the plane of the highest tensile stress substantiates the supposition that the corroding medium will seek out and attack the fibers most highly stressed in tension. There is little reason to assume that the corroding medium will differeniate between a fiber stressed by residual internal stresses and one stressed to the same degree by an external load.

The apparent discrepency in the data so far reported may well be in the method of measuring the internal stress. Scheil slit a short length of tubing, measured the increase in diameter and calculated the internal stress after the method of Sachs and Espey.[20,21] The accuracy of this method of measuring the internal stress depends upon the degree to which the assumption of uniformity of stress distribution across the thin tube wall,

is justified. At best it gives an average of the internal stress for a section 2 - 3 diameters long. The actual internal stress at any point on the surface may well be several times the average value as determined by slitting. The magnitude of the threshold internal stress thus determined will vary, then, depending upon how far the point to point values of the internal stress differ from the average. Elaborate X-ray techniques would be necessary to determine the magnitude of the internal stresses at any spot on the surface. Even X-ray technique will not give the stress at a point but only an average stress over a small area.

An externally applied tensile stress does not produce quite the same stress in each individual grain. It does tend to give a more nearly uniform stress distribution than internal, residual stresses, however. The threshold internal stress as now measured is an average of the individual fiber stresses, some of which may well be considerably higher than the average. It may be reasonably assumed that the corroding medium will attack the most highly stressed fiber first. The values reported for the threshold internal stress required to initiate stress corrosion cracking will tend to vary then, and may be considerably lower than similar values for an externally applied threshold stress.

It would seem sufficient to take the threshold stress as determined by externally loading a bar free

of internal stresses as a measure of the absolute magnitude of the stress required to initiate stress corrosion cracking. The measurement of the internal stress by the Sachs & Espey, or similar methods would serve as a useful index of the amount of cold work, or the cooling rate required to keep the internal stresses below a certain minimum.

It is suggested, therefore, that the work of Franks, Binder, and Brown be extended to include the determination of the magnitude of an externally applied tensile stress necessary to initiate stress corrosion cracking in media other than $MgCl_2$. The specimens to be externally stressed should be free of internal residual stresses. This necessitates slow cooling and limits the investigation to Ti and Cb stabilized 18-8 since it is not desirable to introduce the effect of intergranular attack.

Sheil's work on the magnitude of the internal stress required to initiate stress cracking could be extended to other media. A measured internal stress such as this would be primarily useful as an index of how much stress a given cooling rate or a given amount of cold work introduces.

Measurement of the stress required to initiate cracking in Ti and Cb stabilized 18-8 would furnish the producer and the design engineer with positive, quantitative information as to the effect of stresses on the stress corrosion cracking of stabilized 18-8.

With such clear cut information the 18-8 producer could probably open up an additional large market in the petroleum industry, as Dixon has indicated.[6]

A similar series of experiments could be run on 18-8 sensitized to grain boundary attack, but it would seem best to choose a milder corroding medium. A solution which would cause intergranular stress cracking but would not cause general intergranular attack would be ideal if such a solution could be found. Investigating stress corrosion cracking of 18-8 susceptible to intergranular attack serves primarily an academic interest. Little practical application could result for this type of stress corrosion cracking can be eliminated simply by stabilizing 18-8 against intergranular attack.

It is important to recognize the rarity of stress corrosion failures in austenitic 18 Cr- 8 Ni steel stabilized against intergranular attack. The very difficulty the investigators have had in finding test solutions that will cause stress cracking indicates the generally excellent resistance of stabilized 18-8 to this type of failure. Unfortunately, the occasional failure is often more significant than the ninety and nine cases giving completely satisfactory service. It is particularly difficult to translate laboratory results into field service data. The laboratory tests, of necessity, are made under the severest conditions known, and the effects

of small impurities that may be present in the field service environment are generally neglected.

The Theory of Stress Corrosion

Mears, Brown and Dix have proposed a generalized electrochemical theory of stress corrosion.[5,16] They establish as the two prerequisites of stress corrosion: 1) a susceptibility to corrosion along more or less continuous paths must exist; and 2) a high tensile stress either internal or externally applied must also exist. They picture the material along the more or less continuous paths being anodic to the surrounding metal, and hence rapidly dissolved through the action of the electrochemical potential set up.

The electrochemical theory applies very nicely to many alloys of aluminum, magnesium, copper and to 18-8 sensitized to intergranular attack. These alloys all exhibit a grain boundary precipitate, which is anodic to the surrounding metal. Mears, Brown and Dix have presented some very convincing data showing that, by cathodic protection of sensitized 18-8, stress corrosion cracking in NaCl - H_2O_2 solution could be eliminated.[16] By stretching the electrochemical theory somewhat, it could be made to apply to the transgranular stress cracking of 18-8 stabilized with Ti or Cb and with Ti or Cb carbides at the grain boundaries. The electrochemical theory completely fails to explain the trans-

granular stress cracking of homogeneous, austenitic 18-8 as reported by many investigators.[9,12,21]

Hodge and Miller have pointed out the similarity between a stress corrosion crack and a fatigue crack.[12] No one has tried to evaluate the significance of the chloride ion in the stress corrosion cracking of stabilized 18-8, but in view of the generally poor performance of 18-8 in the presence of chlorine and H Cl, such an approach might be fruitful.

Prevention

Stress corrosion cracking in 18-8 alloys susceptible to grain boundary attack may usually be prevented simply by alloy addition or heat treatment to stabilize the 18-8 against general intergranular corrosion.[21]

Preventing stress corrosion cracking in stabilized 18-8 is the primary consideration of the design engineer and stainless steel producer. The most obvious means of preventing stress corrosion is to stress-relieve. Hodge and Miller found that adequate stress-relief could be obtained by furnace cooling from 900°C. or above.[12] Scheil found that an anneal at 720°C. was effective for 18-8 Cb, but that 870°C. was a better annealing temperature for 18-8 and 18-8 Mo. It is apparently adequate to stress-relieve by slow cooling from 900°C. or above.

Hodge and Miller found that no amount of annealing sufficed to stress-relieve completely a welded joint

joining austenitic 18-8 to a ferritic steel, but that an all austenitic welded joint could be stress-relieved.

It is well to point out that stress-relieving by slow cooling from 900°C. or above is a heat treatment calculated to give maximum carbide precipitation at the grain boundaries. In ordinary 18-8 maximum sensitization to intergranular attack is produced by such slow cooling. Quenching to keep the carbides in solution introduces internal stresses which can cause stress cracking. Therefore, the design engineer is forced to accept the more costly 18-8 alloys stabilized with Ti or Cb and specify slow cooling to the stress free condition at room temperature, <u>if the corroding medium can cause stress corrosion cracking</u>. He should remember that slow cooling may promote the formation of ferrite and therefore a higher nickel or nitrogen content may be advisable, if the presence of a small amount of ferrite is objectionable.

Ingenious, but drastic, quenching of a stainless steel bar so that the outside layers suffered plastic deformation during the quench putting the surface layers under a residual compressive stress has been reported.[9] Such a quench keeps the carbides in solution and prevents stress corrosion, but can develop quench cracks, as Wilcox and Kosting reported.[15] With the surface layer in compression there is no tendency for stress corrosion cracking to occur.[9,12,13,16,21]

Cb, Ti and Mo additions have proved ineffective in preventing stress corrosion.[9,12,21] Riedrich reports that the presence of a small amount of ferrite is beneficial in reducing the tendency of 18-8 to stress crack in $CaCl_2$-$HgCl_2$ solutions.[18] Scheil confirmed this but also found the presence of ferrite had less effect in reducing the tendency to stress crack in $MgCl_2$ solution.[21,22] Scheil has also found that the ferrite stainless steels are nearly immune to stress corrosion cracking.[23] Kalling and Pagels reported that the 23Cr ferritic steels were more susceptible to corrosion when cold worked than when annealed.[14]

Scheil reported that addition of an inhibitor to the medium corroding the autoclave eliminated the trouble.[21] He did not specify either the inhibitor or the corroding medium. The information available indicates the advisability of suspecting the presence of the chloride ion in stress corrosion failures and if possible removing or neutralizing it. There is no guarantee that the absence of the chloride ion will prevent stress corrosion cracking, but it could easily be the source of the trouble.

Before concluding, the possible effect of stress corrosion cracking during etching of microscopic samples should be pointed out. Berge and Schrader have both emphasized the role that stress can play in opening cracks in highly stressed areas during etching.[4,24]

In evaluating fine cracks in 18-8 or any other material as viewed under the microscope, the possibility that they may be stress corrosion cracks initiated by the etching reagent in regions of high stress cannot be overlooked.

Conclusions

1) Stress corrosion cracking can and does occur in austenitic 18 Cr- 8 Ni stainless steel stressed in tension and subjected to the proper corroding medium regardless of the susceptibility to intergranular corrosion, but it is a rare phenomenon.[9,12,21]

2) Failures are characterized by their brittle, localized nature. The surrounding material remains quite ductile.[9,16]

3) Transgranular stress corrosion cracking of stabilized 18-8 has been found to occur in lithium, ammonium, magnesium, zinc, and calcium chloride solutions, in the presence of moist ethyl chloride vapor, and possibly in the presence of naphtha, air, gasoline, and other unspecified media.[10,14,21] Intergranular stress corrosion cracking of 18-8 sensitized to intergranular attack has been found to occur in corrosive media as mild as boiler water and steam.[12]

4) The indications are that a tensile stress about equal to the yield strength at 0.2% offset is required to initiate stress corrosion cracking in

$MgCl_2$ solutions. The measured value of internal stress to initiate cracking is reported by Scheil as 10,000 psi or less.[12,21] The data applies to stabilized 18-8. There is some data to substantiate the supposition that the corroding medium will seek out and attack the most highly stressed fibers first.[16]

5) Internal stresses sufficient to initiate stress corrosion in stabilized 18-8 have been known to result from cold rolling, bending, or even straightening after annealing, also from grinding, welding, and from quenching to keep the carbides in solution.[9,12,21]

6) The electrochemical theory of stress corrosion may apply to 18-8 susceptible to intergranular attack, but cannot apply to the transgranular cracking of the homogeneous, austenitic alloy.

7) When stress corrosion of 18-8, which is susceptible to intergranular corrosion, occurs, it can normally be prevented by rendering the 18-8 immune to intergranular attack.[21]

8) Stress corrosion cracking of 18-8 can be prevented by slowly cooling from 900°C. or above, to stress relieve.[12,21] Such a treatment will sensitize 18-8 to intergranular attack unless the Ti or Cb stabilized alloy is used.

9) Ordinary 18-8 bar stock can be rendered immune to stress corrosion cracking by a drastic quench which leaves the surface layers in compression. The quench will also retain the carbides in solution and prevent

intergranular corrosion, but may initiate quench cracking.[9,15]

10) Ti, Cb, and Mo additions do not prevent stress corrosion failures.[9,12,21] There are indications that a small amount of ferrite may reduce the tendency to stress cracking.[18,21,22]

11) It may be possible to prevent stress cracking when the chloride ion is the active agent in the corroding medium by neutralizing its effect, or by removing it.

12) In interpreting fine cracks under the microscope, the possibility of these being stress corrosion cracks induced by the etchant in highly stressed areas, cannot be overlooked.[4,24]

13) Further investigation to clarify the role of the chloride ion in the stress corrosion failure of stabilized 18-8 is recommended.

14) Investigation to determine the magnitude of the external stress required to initiate stress corrosion cracking of 18-8 Cb and 18-8 Ti in various media is also recommended.

15) It is argued that since methods so far used to determine internal stress values determine only <u>average</u> values, there may be an <u>apparent</u> discrepency between reported values of internal and external stress required to initiate stress corrosion cracking.

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18 Cr - 8 Ni Stainless Steel in High Temperature Service

by

Arthur H. Tuthill

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18 Cr - 8 Ni STAINLESS STEEL IN HIGH TEMPERATURE SERVICE

The purpose of this report is to review the properties and applications of 18 Cr-8 Ni stainless steel and its alloy modifications in high temperature service. Primarily the report deals with the structural stability, physical properties, and typical failures of 18-8 at high temperature--above 300°C. (570°F.). Previous reports have dealt extensively with intergranular and stress corrosion in 18-8. A familiarity with these phenomena is assumed.

18-8 has long been used successfully at high temperatures in steam turbines, parts of gas turbines, condenser, heat exchanger and cracking still tubing, autoclaves, valves, piping, and aircraft exhaust manifolds. Often high pressures as well as high temperatures are encountered. It is the presence of a highly corrosive environment, not the high temperature or high pressure, which usually requires the use of an alloy as expensive as 18-8.

The principal factors that influence the choice of materials for high temperature service are the corrosion resistance and creep strength. Ductility, workability, and weldability are of secondary importance. Thermal expansion, thermal conductivity, specific heat,

density, etc., while important in certain applications, are usually accepted at whatever values are associated with the more critical properties such as corrosion resistance and creep strength.[9,11,35,57]

W. G. Whitman in discussing Dixon's paper has enumerated the properties that would be desirable in an alloy for use in petroleum cracking stills.[9] 1) The alloy must be inherently stable, i.e. its components in equilibrium, in the service temperature range. 2) At service temperature the alloy should have (a) high creep strength, (b) good ductility, (c) adequate impact strength, (d) high thermal conductivity, (e) wear resistance (to withstand the action of brushes in cleaning), (f) high endurance limit, and (g) a co-efficient of thermal expansion similar to that of other alloys with which it may be assembled. 3) The alloy should be easy to fabricate, machine, or weld.[57] The overall cost of the fabricated product must be low. Unless an alloy resists scaling and corrosive attack, an imposing array of physical properties is of little value.

In the final analysis, cost and availability will govern the choice of any particular alloy. The engineer may find that replacing a low cost corrodable material at intervals is more profitable than using of a high cost, less corrodable material such as 18-8.

THE STABILITY OF AUSTENITIC 18-8

Equilibrium Phase Relationships

Austenite is the stable phase in 18-8 only above 900 - 950°C. (1650 - 1740°F.). On slow cooling a carbide phase appears at 900°- 950°C. (1650 - 1740°F.). As 18-8 is further cooled to 600 - 650°C. (1110 - 1200°F.) ferrite can form. At room temperature the equilibrium phases are ferrite and carbide.[26] A pseudo-equilibrium diagram showing the approximate relationship of phases is included as Page A of the appendix.

The precipitation of the carbide is slow except in the 750 - 900°C. (1380 - 1650°F.) range. Carbide precipitation can easily be avoided by quenching. The transformation of austenite to ferrite is an even slower process than the precipitation of carbide. It is difficult to produce completely ferritic 18-8, in fact. It can only be done by long time holding at the transformation temperature, or by complete elimination of nitrogen from the analysis.[26, 51]

Commercial practice is to quench 18-8 from above 900°C. (1650°F.), thus maintaining homogeneous austenite untransformed down to room temperature.[26] Although the austenite is unstable, it can be maintained indefinitely at room temperature. Cold work and an increase in tem-

perature both tend to transform the unstable austenite to the more stable structure, ferrite and carbide.

High Temperature Ferrite

Ferrite has been referred to as the stable, equilibrium phase at room temperature. In the presence of sufficient chromium, titanium, molybdenum, tungsten, silicon, vanadium or columbium, ferrite may be stable and coexist with austenite at temperatures above 900°C. (1650°F.) [15,37,41,48] The ferrite forming elements have a dual function. They increase the tendency to form a two phase alloy with some stable ferrite present at all temperatures and they also increase the tendency for austenite to transform to the equilibrium structure, ferrite, below 650 - 600°C. (1200 - 1110°F.).

Uhlig maintains that in the absence of nitrogen 18-8 is completely ferritic.[51] Increasing the nickel or nitrogen content will stabilize the austenite and tend to produce a single phase, homogeneous structure.[15,24,51]

Sigma Phase

There is evidence that ferrite is not completely stable in alloy modified 18-8. Schafmeister and Ergang developed an Fe-Cr-Ni constitution diagram which shows the limits of the brittle, non-magnetic sigma phase, Appendix, Page B.[45] The position of 18-8 on this diagram

is indicated by a triangle ( ). It will be noted that at 8% Ni it would require not 18, but 22% Cr to place the composition in the nearest phase field where sigma could form. In the absence of alloying elements, the formation of sigma phase in ordinary 18-8 should not occur.

Increase of the chromium content to 22%, addition of 2 - 4% Mo, addition of varying amounts of titanium, tungsten, silicon, tantalum, zircromium, aluminum and columbium are known to cause the formation of sigma phase in 18-8.[1,2,15,41,42,48] It seems reasonable to suppose that any alloy addition that promotes the formation of ferrite, also promotes the formation of sigma.

There is considerable discussion as to just how sigma forms. The formation of sigma is often followed magnetically.[45] Austenite is non-magnetic; ferrite, magnetic; sigma, non-magnetic. The amount of ferrite formed from austenite can be estimated by the increase in magnetism. After equilibrium between austenite and ferrite has been established, the formation of sigma may be followed by the loss in magnetism.

Riedrich states that sigma is most often observed to form from ferrite in his paper.[41] In the discussion he exhibits microstructures showing the formation of sigma directly from austenite in reply to M. Schmidt of Dusseldorf who maintained the opposite.

Embrittlement

18 Cr-8 Ni stainless steel and its alloy modifications are not susceptible to the temper brittleness associated with the plain chromium and lower alloy steels.[21,41,56,57,58] Temper brittleness in plain chromium and low alloy steels occurs in the 400 - 600°C. (750 - 1100°F.) range and apparently is a precipitation phenomena.[21,25,42] Embrittlement of 18-8 does occur, but it is not related to the more common temper brittleness of ferritic alloys.

Ordinary 18-8 on slow cooling or on holding for short periods of time in the 700 - 900°C. (1290 - 1650°F.) range suffers embrittlement by the precipitation of carbides at the grain boundaries.[4] Carbides precipitate at much lower temperatures but are so finely divided that they have no embrittling effect. At higher temperatures, 700 - 900°C. , the carbides are coarser and lower the impact strength. It should be emphasized, that even after maximum carbide embrittlement has occurred the impact strength is still at a very high value, 40 ft.-lbs. Izod.[4] Riedrich states that carbide embrittlement can be eliminated by use of Cb or Ti stabilized alloy.[41]

Riedrich emphasizes the embrittlement that can occur on long exposure to high temperatures.[41] Since ordinary 18-8 does not have enough chromium to form sigma, this type of embrittlement will usually be confined to the

alloy modifications of 18-8.[45] Franks, Binder, and Bishop found that 2 - 4% Mo added to 18-8 caused sigma to form.[15] Titanium is known to favor the formation of sigma and it is a strong ferrite former.[37, 48] Columbium, while it favors both ferrite and sigma formation is relatively weak compared to Ti and Mo.[4,15] This gives columbium stabilized 18-8 a slight advantage for high temperature service. If embrittlement by sigma formation has occurred, heating to 920°C. (1690°F.) will dissolve the sigma phase.[45]

Cold Work, Recrystallization, and Stress Relief

18-8 can be cold worked and recrystallized as any other homogeneous alloy. Recrystallization occurs in the temperature range 1000 - 1200°C. (1830 - 2190°F.)[29] Because austenitic 18-8 is in unstable equilibrium at room temperature, cold work actually causes some transformation of austenite to ferrite. Cold work also causes a marked increase in the rate of precipitation of carbides on reheating above 400°C. (750°F.).

Sigma redissolves above 920°C. (1690°F.); carbide, above 900°C. (1650°F.); and ferrite, above 900 - 950°C. (1650 - 1740°F.). It is clear that no matter what happens to the metastable austenite below 900°C. (1650°F.), on reheating to recrystallize, the normal structure will be homogeneous austenite before the recrystallization range

is reached. Heating above the recrystallization range causes rapid grain growth.[34]

The temperature at which full stress relief may be obtained can be deduced from the work of Scheil and the work of Hodge and Miller on stress corrosion of 18-8. Scheil and Hodge and Miller reported that furnace cooling from 875 - 900°C. (1610 - 1650°F.) was required to keep residual stresses low enough to give immunity to stress corrosion in $MgCl_2$ solution.[20,46] It may be concluded that in order to get complete stress relief, 18-8 must be heated to 900°C. (1650°F.) and furnace cooled.

Austenitic vs. Ferritic Structure

Many of the mechanical properties of 18-8 are directly related to the homogeneous austenitic structure. The excellent ductility and good toughness at high tensile and yield strengths are in large measure attributed to the austenitic structure.

Austenite is not truly stable below 900 - 950°C. (1650° - 1740°F.) but can easily be quenched to room temperature and maintained indefinitely. When 18-8 is to be used at high temperatures, the possibility of ferrite formation and carbide precipitation must be reckoned with. If the Ti, Mo, or Cb alloy of 18-8 is being considered, the possibility of sigma formation cannot be overlooked.

Carbide precipitation sensitizes the 18-8 to

intergranular attack unless the Cb or Ti stabilized alloy is used. In the temperature range 700 - 900°C. (1290 - 1650°F.) the precipitated carbides actually embrittle 18-8, but not seriously. Serious embrittlement can occur on long time holding at temperatures below 920°C. (1690°F.) if the Mo, Cb, or Ti content is too high.[1,15,41] Ferrite causes hotshortness.[41] The presence of small amounts of ferrite do decrease the susceptibility to intergranular corrosion.[37] It is possible that the formation of ferrite in 18-8 cracking still tubes may lead to brittle failures.[6] The presence of ferrite destroys the homogeneity of austenitic 18-8 and is generally to be avoided. The new ferritic 18-8 + Ti + Al age hardening alloy recently developed may serve as a yardstick to compare the properties of ferrite to those of austenite in 18-8.[48]

CORROSION RESISTANCE OF 18Cr -8 Ni STEEL

The Oxide Film

The excellent corrosion resistance of 18 Cr- 8 Ni stainless steel is usually attributed to the formation of a thin, tightly adhering film, ordinarily a chromium oxide scale. Forrest, Roetheli, and Brown showed that the initial rate of corrosion of film free 18-8 in water of known oxygen content was very high and of the same order of magnitude as that of a plain carbon steel.[14] As the film formed, the rate decreased and quickly leveled off. Stockdale and Evans actually removed a film from the surface of 18-8 and studied it.[12] Other theories of corrosion have emphasized the electrolytic aspect. Uhlig and Wulff have gone so far as to develop a specialized electron sharing theory of passivity applicable only to 18 Cr- 8 Ni stainless steels.[52] For the purposes of this paper it is simpler to discuss the corrosion problem in terms of the oxide film theory, remembering that electrolytic effects are ever present and ever important.

Accepting the oxide film theory and considering what happens in air, the following picture is drawn. The oxygen of the air reacts with the chromium of the 18-8 and forms a thin, tightly adhering film of chromium oxide on the surface. Further corrosion is prevented by the resistance the film offers to the diffusion of iron outwards and the diffusion of oxygen inwards. The film probably contains some iron and nickel oxide, but it is the chromium oxide

which is important.[3,29,30,40,41,54]

If oxygen is not available, as in a reducing atmosphere, the oxide film can not form. If previously formed, it may be reduced. In either case the 18-8 is no longer protected by its oxide film. The corrosion resistance will depend upon the extent to which the reducing atmosphere attacks 18-8 and the character of the film or scale that may be formed. Often nickel is more effective than chromium in limiting corrosive attack in reducing atmospheres, except where sulphides are present. In general 18-8 is resistant to corrosion in strongly oxidizing atmospheres, but is often severely attacked in a reducing atmosphere.[3,29,40,54]

Scaling in Air at High Temperatures

At high temperatures corrosion resistance is of primary importance. In air 18-8 begins to show loss of weight after long periods at 760°C. (1400°F.), but the loss is still small at 870°C. (1600°F.). Corrosion increases more rapidly at higher temperatures.[40,56,57,58] At 870°C. (1600°F.) manufacturers report the gms. weight loss per sq. inch after 168 hours heating as less than 0.05.[58] Cb and Ti additions do not affect the scaling in air appreciably, nor do they affect the resistance to other corroding media.[54,58]

Corrosion in Steam

The resistance of 18-8 to corrosion in high temperature steam has been studied by several investigators.[16,18,43,49] Hawkins, Agnew, and Solberg found 18-8 and 18-8Cb started to corrode rapidly above 915°C. (1675°F.).[18] Rohrig, Van Duzer and Fellows found 18-8 to pit at 595°C. (1100°F.) in steam.[43] Fuller in discussing 18-8 for turbine service, draws attention to the possibility of erosion by high velocity droplets.[16] Little good data is available on erosion, especially high temperature erosion, but it can be a very important factor in piping, pump and still design.

Corrosion in Reducing Atmosphere

Reducing atmospheres, particularly when chloride or sulphide ion is present, are destructive to chromium bearing steels.[2,3,29,35,40,41,54] The addition of Mo and an increase in the nickel content increase the resistance of 18-8 to attack by the chloride ion. Sulphur, as H_2S, attacks 18-8, sulphur combining with the nickel to form a low melting eutectic (M.Pt.645°C.). At temperatures above 645°C. (1190°F.), this low melting constituent loosens the scale and exposes fresh metal to further attack.[29,35,40,54] Molybdenum addition and the substitution of manganese for nickel improves the resistance of 18-8 to attack by sulphides in a reducing atmosphere.

The effect of sulphur in an oxidizing atmosphere, as for example SO_2, is much less severe. If the atmosphere is strongly oxidizing, the 18-8 can be fully resistant below 650°C. (1200°F.) even though SO_2 is present.[29,41] Rickett and Wood have shown that in the plain chromium steels, increasing the chromium content has little effect on scaling in a H_2S atmosphere at 760 - 1090°C. (1400 - 2000°F.).[40] The scaling of 18-8 in H_2S cannot be attributed entirely to the formation of nickel sulphide, then.

The presence of sulphur and the type of atmosphere, oxidizing or reducing, are important in determining the suitability of 18-8 for a particular application. It is interesting to note that according to Mead, Schaffer and Camp, ordinary 18-8 tubes have given long and satisfactory service in cracking a high sulphur content oil at temperatures of 425°C. (800°F.).[32]

Resistance to H_2 and NH_3

Leihener, Grun and others report that 18-8, 18-8-Ti and 18-8-Mo are resistant to embrittlement by H_2 or NH_3 at 550°C. (1020°F.) and 600 atmospheres.[29,56] Rhodes reports that H_2 used in the synthesis of NH_3 at 450 - 500°C. (750 - 930°F.) decarbonizes chromium steels.[39] Since low carbon 18-8 is highly desirable decarburization would not prevent the use of 18-8 in such an application.

Intergranular Corrosion

An important consideration in the use of 18-8 at high temperature is the susceptibility to intergranular corrosion. The first report of this series dealt extensively with intergranular corrosion. When 18-8 is reheated to 400°C. (750°F.) or above and held for long periods of time as in continuous high temperature service, carbides will form and precipitate at the grain boundaries. If the medium to which 18-8 is exposed will attack 18-8 thus sensitized, intergranular attack and failure result.

The importance of the corrosive medium cannot be minimized. The corrosion resistance of 18-8 even in the sensitized condition is remarkable. The oil industry has used thousands of 18-8 tubes satisfactorily for many thousands of hours at temperatures within the sensitization range.[6,9,32] Obviously, if the corrosive medium will not attack sensitized 18-8 at elevated temperatures, there is no reason to go to the more expensive columbium and titanium stabilized alloys. If the corrosive medium does attack sensitized 18-8 and the service temperature is above 400°C. (750°F.), either the columbium or titanium stabilized alloy must be used to prevent intergranular attack.

Carburization

Carburization of 18-8 may lead to failures in certain high temperature applications. There is little use in

selecting a columbium or titanium stabilized 18-8 if carburization occurs under service conditions. Titanium or columbium is added to 18-8 to keep chromium from combining with the carbon present. If carbon is added by carburization, the effect of the titanium or columbium is nullified. The chromium can combine with the carbon added and precipitate at the grain boundaries thus sensitizing 18-8 to intergranular attack. Carburizing 18-8 can also have an embrittling effect for the carbides are concentrated at the grain boundaries.[22,24,30]

Hydrocarbon gases above 700°C. (1300°F.) can carburize austenitic 18-8, according to Lincoln.[30] 18-8 Mo after 160 hours at 980°C. (1800°F.) in a carburizing atmosphere had in excess of 0.45% C in the case and a 0.4 in. case depth. 18-8 after the same treatment had about 0.2% C in the case and a 0.25 in. case depth.[30]

Kahn and Huebel have both reported what they believe to be carburization of 18-8 Cb and 18-8 Ti aircraft exhaust manifolds.[22,24] Some carburization has been detected in 18-8 oil still tubes that failed.[57] Kahn, Oster, and Wachtell pack carburized 18-8 Ti samples to a case depth of 0.02 inches in 3 hours at a temperature slightly above 700°C. (1300°F.). Riedrich refers to the carburization of 18-8 as "dry intergranular corrosion."[41]

Riedrich and Lincoln report that the presence of ferrite decreases carburization and that high chromium,

ferritic steels are not susceptible to carburization.[30,41] Kahn and his co-workers report a copper coating effective in preventing carburization.[24] Silicon alloy addition decreases carburization markedly.[30]

Carburization of 18-8, then, can be a factor in high temperature applications. It destroys the immunity to intergranular corrosion in the columbium or stabilized alloy.

Resistance to Attack by Molten Metals

Molten metals, fused salts, glasses, tobin bronze, zinc, and mercury all attack 18-8 intergranularly.[19,29] 18-8 cannot ordinarily be used at high temperatures in contact with these materials. At lower temperatures mercury is the sole offender of this group. If 18-8 is to be used, the temperature must not only be held below the melting point of the metal or salt but also below the temperature at which appreciable diffusion will occur.

Corrosion Resistance in Other Media

The corrosion resistance of 18-8 to other media at high temperature such as acids, bases, and hydrocarbons will not be included in this report. Zapffe has collected and compiled the data on corrosion resistance of 18-8 in various liquids at various temperatures.[54]

Effect of Alloy Additions

The general corrosion resistance of 18-8 is not significantly affected by columbium or titanium additions. Molybdenum was first added to 18-8 in the hopes that it would prevent intergranular attack. It did not, but it was found that molybdenum increased the resistance of 18-8 to pitting, to attack by the chloride ion, and to attack in a reducing atmosphere.

Up to this point the molybdenum alloy has been referred to as an 18-8 alloy. Actually, the most useful alloy for high temperature service is a 16 Cr- 13Ni - 3 Mo steel. The chromium content has been reduced and nickel content increased to stabilize the austenite and prevent the formation of ferrite and sigma. 18-8 with about 2% Mo is still widely used at low temperatures because of its excellent corrosion resistance. The 18 Cr- 8 Ni- 2 Mo alloy will not be considered further in this report.

HIGH TEMPERATURE PHYSICAL PROPERTIES

Creep

Creep in metals generally refers to the very slow, permanent deformation that can occur at constant stress (i.e. below the instantaneous value of yield strength) at high temperatures. There are two important problems that depend upon the creep characteristics of metals. First, what is the maximum stress that can be sustained without rupture over the service life, 1, 2, 5, 10 or 20 years? Second, what is the maximum stress that can be sustained without the permanent elongation exceeding a given design limit over the service life, 1, 2, 5, 10, or 20 years?

Before considering 18-8 specifically, a more general picture of creep in metals will be presented. The nature of creep demands that experiments be run over the full service life of the proposed installation. The time and effort involved tempted investigators to develop a suitable short time test that will provide reliable design data. The two most widely used short time tests are the high temperature tensile test in this country, and the D V M test A 117 in Germany. These tests are useful only in giving broad indications as to the creep characteristics of metals. A great deal of evidence has been compiled showing that the results of the high temperature tensile test and D V M test A 117 bear no consistent relation to

the results of long time tests or to service experience.[11,13,38,41,47] The current trend in creep testing is towards the long time full life creep tests.

Creep tests are made on specimens loaded in tension at a controlled temperature. The elongation of the specimen is measured and plotted as a function of time. A typical time elongation curve is included in the appendix, Page C. When first loaded, the specimen stretches rapidly. If the stress is not too high, the rate of elongation gradually decreases and finally settles down to a relatively constant rate. After deforming at a constant rate for considerable time (thousands of hours), the rate begins to increase once more and elongation increases rapidly to failure. The curves on Page C of the appendix illustrate the three stages of creep. Curve (1) shows all three stages. Curve (2) has not been extended far enough to reach stage three.

The typical time-elongation curves on Page C also illustrate the method of measuring the minimum creep rate as the tangent to the curve during stage two. A unit rate of 10^{-6} in/in at 1000 hours (0.1% in 1000 hrs.) is also illustrated. The stress which gives this unit rate during stage two is taken as a measure of the creep strength for design work in this country. An actual time elongation curve for an undesignated material is included as Page E of the appendix.[57] It illustrates very clearly the necessity for long time tests to establish with any

certainty the minimum creep rate characteristic of stage two. Not until 3000 hours does the creep rate settle down to a constant value. Much of the data in the literature has been obtained on tests lasting considerably less than 1000 hours. Time-elongation curves are determined at constant temperature and constant stress. By measuring the minimum creep rate during the second stage on a series of time-elongation curves for constant temperature and different stresses, a plot of the stress vs. creep rate is obtained. Such a curve for 18-8 is included as Page E of the appendix. It is usually plotted on log-log paper in order to approximate a straight line relationship. Ordinarily a series of lines are plotted for different temperatures.

From a series of stress vs. creep rate curves for various temperatures, the creep strength may be determined and plotted as a function of temperature, Page F of the appendix.

The creep strength has been variously defined as the stress which gives a creep rate of 0.1% per 1000 hours (1% per 10,000 hours), also as the stress which gives a creep rate of 0.01% per 1000 hours (0.1% per 10,000 hours or 1% per 100,000 hours).[11,38,55,56,57,58] Since few tests are run over 1000 hours, the values at 10,000 and 100,000 hours are generally extrapolated. The German D V M test A 117 measures the creep strength as the stress

which will produce an average creep rate of 4-5 x 10^{-4}% per hour during the 25th to 35th hour interval of a 45 hour test.[38,41,47] In England the creep strength is often defined as the stress which will produce a creep rate of 1 x 10^{-3}% per day or 0.4 x 10^{-4}% per hour on the 40th day (960 hours) of the test.[38]

The older literature defined the creep strength as the maximum stress below which the initial creep comes to a stop.[38] It is generally accepted now that creep does not come to a stop, simply settles down to a constant rate during the second stage.[2,11,25,29,30,38,47,50]

Theory of Creep

The exact mechanism by which a metal "creeps" is the subject of considerable discussion and controversy. Although Rosenhain's amorphus cement theory has been generally discarded, his conception of a definite temperature where the strength of the metal across the grain boundaries was equal to the transgranular strength has been retained by many investigators. Above this temperature intergranular failures are assumed to occur; below this temperature transgranular failures occur. Such a temperature is called the equicohesive temperature.[36,47,50] There is no good data to show that such a temperature exists. Siebel and Hahn point out that the very data Thiekman and Parker base their statements about the equicohesive temperature on shows the tremendous influence of composition on the type of fracture.[47]

The most promising theories of creep have been developed by Kanter and by Seibel and Hahn.[25,47] Siebel and Hahn emphasize that the overwhelming majority of creep data has been obtained on low alloy heat resisting steels in the temperature range 450 - 650°C. (840 - 1200°F.) which is the range in which recovery and recrystallization occurs. They draw attention to the fact that precipitation, diffusion, atomic rearrangements, and translation as well as recrystallization and recovery affect the creep strength of a metal in this temperature range.

Siebel and Hahn regard the sudden increase in the minimum creep rate of the second stage above a narrow range of temperature or stress as significant. Below the recovery temperature, they maintain that creep occurs by a process of atomic rearrangement in the grain boundaries at low stresses, and by translation at higher stresses. In the recovery and recrystallization range atomic rearrangement in the grain boundaries is supplemented by atomic rearrangement within the grains at low stresses. At higher stresses slip planes form within the grains. Above the recovery and recrystallization range, grain boundary atomic rearrangement predominates at low stresses, aided by translation at higher stresses. Siebel and Hahn explain the decrease in creep rate during first stage as the result of strain hardening by translation.

Kanter suggests a similar but somewhat more detailed theory of creep.[25] Inhomogeneity from grain to grain is assumed. When first loaded, those grains with lower yield strengths deform first. As they deform there is a tendency to shift the load to adjacent grains. Work hardening increases the yield strength of the initially weaker grains. Thus during the first stage there is a succession of events, plastic deformation of the grains, stress redistribution among the grains, and increase in strength of the weaker grains by work hardening.

The second stage with a minimum creep rate sets in when strain hardening and stress redistribution have evened out the initial inhomogeneities. It is proposed that creep proceeds by shear with strain hardening, and stress readjustments remaining constant. It has been shown that creep in single crystals of lead proceeds by means of slip along crystal planes subjected to maximum shear stresses.

The third stage is pictured as the result of a preferred orientation developing which places the potential slip planes in better alignment with the planes of maximum shear stress. Such a realignment would be aggravated by necking down. Actual rotation of the grains has been demonstrated in a tin-lead alloy.

Kanter points out that grain rotation would be expected to produce intergranular failures, whereas strain hardening would produce intragranular failures. He concludes that the type of failure is a function of the rate of straining.

An interesting calculation for a creep rate of small magnitude about (0.01% per year) indicates that slip should occur on planes at discrete intervals of atomic pitch about once an hour. The metal is pictured as being in a state of elastic strain essentially, but disturbed occasionally by slip. Each disturbance causes a stress redistribution and lays the ground work for the next disturbance.[25]

Parker believes that the deformation at the grain boundaries during creep causes minute imperfections on the atomic scale, which, under the influence of tension, grow to microscopic size with the passage of time and initiate failures.[36]

The Effect of Certain Factors on Creep

Grain size is known to influence creep strength. Above the recrystallization temperature coarse grained steels show higher creep strength. Below the recrystallization range fine grain steels show higher creep strength.[47] Newell has shown that increasing the grain size of 18-8 adversely affects the physical properties at temperatures in the range 425 - 925°C. (900 - 1700°F.).[34] These temperatures are below the recrystallization range.

It has been generally observed that alloys with high recrystallization temperature have better creep characteristics. The function of alloying elements may be largely accounted for as they modify the temperature of recrystallization.

Molybdenum has proved most valuable in increasing creep strength of steels.[41,47] Clarke and White emphasize the fact that an alloy addition must be uniformly distributed to realize its full effect on creep strength.[7] They point out that with segregation the weakest portion of the metal will determine the overall creep characteristics. This is undoubtedly true and is not at variance with Kanter's theory of inhomogeneities from grain to grain. The inhomogeneity occasioned by segregation to which Clarke and White refer is on a microscopic scale where appreciable areas have lower properties than other areas.

Curves G and H of the appendix show the influence of columbium and molybdenum on the creep strength of 18-8. Columbium increases the creep strength below 650°C. (1200°F.).[11,41,57] Molybdenum increases the creep strength below 760°C. (1400°F.)[11,41,56,57] Titanium has no effect on the creep strength of 18-8.[57,58]

The effect of temperature fluctuations on creep testing has been demonstrated by Fellows, Cook, and Avery and by Brophy and Furman.[5,13] Fellows, Cook, and Avery found that a 25 Cr- 12 Ni steel sample tested at 982°C. (1800°F.) under a 3000 psi load developed a 4.5% residual elongation in 221 hours when temperature was allowed to fluctuate between 977°C. and 988°C. (1790°F. and 1810°F.).[13] Brophy and Furman using an 18-8 + Cb alloy at 982°C.(1800°F.) discovered that cycling the temperature to (870°C.) 1600°F.

increased the total elongation by as much as 200% before the normal creep rate was resumed.[5] It is worthy of note that at the temperatures at which these observations were made, it is quite probable that both the 25-12 and 18-8 alloy were already in the third stage of rapidly increasing creep rate.

The Rupture Strength

Present investigations of creep characteristics have led to the redevelopment of the original "overloaded creep test" or the "stress-to-rupture test." The specimen to be tested is loaded in tension and the time to failure noted. On a series of specimens loaded to different stress values, the time for rupture is approximately a straight line on log log paper.[2,47,50,53] A typical stress rupture curve for 18-8 is included as Page I of the appendix.

It will be noted that the short time tensile strength serves as the origin of the stress rupture curve. Such curves are a clear indication of the futility of attempting to use the short time tensile properties for design data. The break in the curve at 90 hours results from intergranular oxidation as first pointed out by White, Clarke and Wilson.[53]

Thielemann and Parker attempted to associate the break in the curve with the "equicohesive temperature."[50] Avery, Cook, and Fellows point out that a series of stress-rupture and creep strength vs. stress curves provide the engineer

with the best design data available.[2] The danger of extrapolating the stress rupture curves to determine maximum life is obvious. Since intergranular oxidation may occur at any time and greatly shorten the expected life, tests must be run long enough to determine the straight line portion after intergranular oxidation has set in. This has not often been done and stress-rupture data must be used with care for this reason.

From a series of stress-rupture curves at different temperatures the stress required to obtain rupture in 1000 hours may be plotted as a function of temperature. The stress to rupture at 1000 hours can usually be obtained with fair accuracy. Extrapolation to 100,000 hours yields data that may have little actual significance. Stress-rupture data extrapolated to 100,000 hours is used as a measure of the expected life, however. When used in conjunction with the creep strength, it gives the best information at present obtainable, short of the full life experimental data.

Stress-to-rupture in 1000 hours has been plotted as a function of temperature for 18-8, 18-8 Cb, and 16-3-3 as Page J of the appendix. Stress-to-rupture extrapolated to 100,000 hours has been plotted as a function of temperature for the same materials as Page K of the appendix. Columbium is seen to increase the stress required for rupture in 1000 and 100,000 hours, but not so much as the molybdenum addition. The effect of columbium is more

significant when it is remembered that less than 1% Cb is actually present and much of this is not dissolved in the matrix but present as a carbide at the grain boundaries. No data for stress rupture is available for the titanium alloy. In view of the fact that titanium had no effect on the creep strength, it seems safe to assume it will have little if any effect on the stress-rupture strength.

Fatigue

Fatigue of 18-8 at high temperatures has not been extensively studied. Fuller gives the endurance limit in steam at 150°C. (300°F.) as 34,000 psi for 18-8 in the fully annealed condition.[16] After holding at 650°C. (1200°F.) for 500 hours, the endurance limit had dropped to 21,000 psi presumably because of carbides that precipitated in the grain boundaries.

Evans gives a curve for endurance limit of 304 in air up to 650°C. (1200°F.).[11] This curve is included as Page L of the appendix.

The Coefficient of Linear Expansion

The coefficient of linear expansion increases with temperature. At 650°C. (1200°F.) the coefficient of expansion for 18-8 is 11.16 x 10^{-6} inches per inch.[57] This is about 50% lower than the handbook value for the coefficient of expansion for plain carbon steel, 16 x 10^{-6}.

The variation of the coefficient with temperature for 18-8 is plotted as Page M of the appendix. Page N of the appendix is a table of the average value of the coefficient over the temperature ranges indicated. Average values were available for 18-8 + Cb and 16-13-3 as well as 18-8. The alloy content slightly lowers the expansion coefficient but the effect is only of the order of 3-4%.

Thermal Conductivity

The thermal conductivity of 18-8 is low, about 100 BTU/sq.ft./hr./°F./in. at room temperature.[11,58] It increases slightly with a rise in temperature. Columbium and molybdenum additions do not affect the thermal conductivity appreciably at low or high temperatures. All values of the thermal conductivity (K) for 18-8, 18-8 + Cb, and 16-13-3 fall within the band indicated on the graph page (O) of the appendix.[11,58] The thermal conductivity of other steels has been included for comparison. No data is available for the 18-8 + Ti alloy.

Specific Gravity, Damping Capacity

Evans records the specific gravity of 18-8 as 7.90; of the columbium and molybdenum modified 18-8 as 8.00.[11]

The damping capacity is the ability of an alloy to absorb vibrational energy thru molecular friction and "damp out" vibrational stresses. The damping characteristics of the austenitic alloys, as 18-8, are poor above 480°C. (900°F.).

FAILURES OF 18 Cr - 8 Ni STEEL IN HIGH TEMPERATURE SERVICE

Failures of 18-8 at high temperature occur from a variety of causes. Overheating, overstressing, excessive erosion from mechanical tube cleaning, and insufficient allowance for expansion and contraction are major causes of failure.[35] An extreme example of such failures is recorded by Babcock & Wilcox where 18-8 tubing was grossly overheated and failed thru bending stresses set up.[57] Proper operation and design will correct such failures.

Carburization, sulphidization, oxidation, intergranular corrosion, pitting, pressure or temperature fluctuations, and possibly stress-corrosion acting singly or in combination cause high temperature failures in 18-8.[9,10,22,24,30,35,41,44,57] Structural changes may likewise cause or contribute to failures. Carbides precipitating at the grain boundaries sensitize 18-8 to intergranular attack and cause slight embrittlement.[4] Clark and Freeman believe that the formation of ferrite directly contributes to brittle failures.[6] Sigma phase may form in alloy modified 18-8.[1,15,45]

Carburization

There is abundant evidence of carburization being a primary as well as secondary cause of failures in 18-8 at high temperatures. Kahn, Oster, and Wachtell report failures

in aircraft exhaust manifolds due to carburization of the 18-8+Ti stabilized alloy.[24] Hubbell reports the same type of failures in ordinary 18-8 frequently, in 18-8+Cb and 18-8+Ti occasionally.[22] Babcock and Wilcox give three different examples of carburization associated with failure of cracking still tubes.[57]

Riedrich in Germany and Lincoln in this country both emphasize the importance of possible carburization in high temperature service applications of 18-8.[30,41] Lincoln points out that hydrocarbon or other gases containing carbon can carburize 18-8 above 1300°F.[30] It is important to realize that any gas or other material which leaves a soot deposit high in carbon is potentially carburizing. The carbon in the soot deposit can easily be oxidized to CO under the influence of high temperature and oxygen in the air. Thus local concentrations of CO in a soot deposit may exist and carburize 18-8 even when the atmosphere surrounding the soot deposit is neutral or even decarburizing. It is the concentration of CO or hydrocarbon in contact with the 18-8 that determines whether carburization occurs.

Carburization can be prevented by electroplating a thin layer of copper on 18-8.[24] It is possible that removing any soot deposit that formed would prevent or at least decrease carburization from combustion gases. These gases usually contain considerable amounts of CO_2 and water vapor;

hence, in the absence of a soot deposit would normally be decarburizing.

Intergranular Oxidation

Intergranular oxidation can cause failure of 18-8 at temperatures above 870°C.(1600°F.) by scaling.[40,58] White, Clark, and Wilson found that intergranular oxidation after about 100 hours at 815°C.(1500°F.) gave a sharp break in the stress vs. time for rupture plot. (See Page I, appendix.) Clark and Freeman believe that intergranular oxidation may initiate cracking and permanent embrittlement in the 18-8 tubing they studied.[6] Kahn and his co-workers and Hubbel recognized that oxidation as well as carburization occurred and undoubtedly contributed to failure of the 18-8 exhaust manifolds.[22,24] Babcock and Wilcox indicate that oxidation contributed to one of the three failures of 18-8 tubing listed.[57]

Above 875°C.(1600°F.) 18-8 may fail by scaling. Between 760°C.(1400°F.) and 875°(1600°F.) the slight oxidation that can occur may accelerate failure due to other causes.

Pitting

Dixon in the Book of Stainless Steels shows an example of an 18-8 tube that failed by pitting at 345°C. (650°F.) Corrosive attack of 18-8 usually is localized

pitting, not general scaling. Pitting is greatly reduced by molybdenum additions.[15,28,37]

Submicroscopic Cracks

Clark and Freeman studied 18-8 cracking still tubes that had been in service up to 100,000 hours at 650 - 675°C. (1200 - 1250°F.)[6]. They found some tubes that were brittle but that could have their ductility restored by rejuvenation treatments at 815°C. and 1040°C. (1500°F. and 1900°F.). Other brittle tubes could not be restored to a ductile condition by any heat treatment.

These investigators found a precipitate at the grain boundaries of embrittled tubes. The magnetic response and microstructures indicated ferrite to be the grain boundary precipitate. The difference in the coefficient of expansion of ferrite and austenite provided the authors with a theory to explain the observed facts.

Highly alloyed ferrite particles precipitate at the grain boundaries and grow to appreciable size. Carbides also precipitate at 650 - 675°C. (1200 - 1250°F.), but as Becket and Franks have shown are very fine and difficult to resolve under the microscope.[4] Clark and Freeman suggest that the embrittlement which cannot be removed by heat treatment results from formation and propagation of fine cracks in the ferrite. The cracks are believed to form during heating and cooling cycles, primarily due to the difference in the coefficients of expansion.[6]

It is interesting to consider the possibilities of such a mechanism of failure further. At service temperatures, 650 - 675°C. (1200 - 1250°F.), ferrite precipitates. Since ferrite has a larger volume than austenite, the austenite surrounding the particle of ferrite is pushed back and may plastically deform. The ferrite cannot expand to its free volume but will seek a compromise and remain in compression.

Now when the cracking still is shut down for cleaning, the temperature is decreased. The ferrite, since it has a lower coefficient of expansion, contracts less on cooling than does the austenite.[35] The ferrite is thus compressed still more during cooling and undoubtedly deforms plastically in compression. On reheating after cleaning, the austenite expands most. If the ferrite suffered considerable plastic deformation in compression, a relatively low temperature will suffice to relieve all remaining elastic, compressive stresses in the ferrite. As the temperature is further raised towards service temperature the ferrite must stretch in tension. First it stretches elastically, then plastically. If the ultimate strength is exceeded at any point before service temperature is reached, a submicroscopic crack will form and propagate. Such a crack cannot be removed by any heat treatment.

Other failures

The three failures listed by Babcock and Wilcox were attributed to (a) overheating due to excessive coking, (b) overstressing during heating and cooling cycles, and (c) overheating and bending stresses.[57] C. C. Snyder in discussing Dixon's paper attributed most of some 20 known failures to overheating.[9] C. P. Miller in discussing Clark and Freeman's paper records some 25 failures which he believes similar to those studied by Clark and Freeman.[6] E. R. Wilkinson does not specify the number of failures in discussing the same paper but believes the mechanism is essentially as proposed.[6] Dixon mentions sudden brittle failures at low and high temperatures which may well be stress corrosion failures.[10] It is to be noted that complete stress relief is not obtained below 900°C. (1650°F.)

Failures of 18-8 in high temperature service have been dealt with in this report. It is well to remember that failures are rare and the metallurgist and design engineer must carefully evaluate their significance in order to obtain maximum usefulness from 18-8. Mead, Schaffer and Camp, Snyder, Miller and others have pointed out that the tubes that have failed are outnumbered a thousandfold by tubes giving satisfactory service.[6,9,32] It is particularly interesting to note that Clark and Freeman found two tubes which had operated 97,000 hours at temperatures where maximum sensitization to grain boundary attack occurs,

650 - 675°C. (1200 - 1250°F.). The only possible conclusion, since Clark and Freeman found specimens from these tubes susceptible to intergranular attack in the Strauss test, is that petroleum containing sulphides is not sufficiently corrosive at high temperatures to cause intergranular attack. The danger in overemphasizing failures and laboratory test results is thus apparent.

CONCLUSIONS

1. Below 760°C. (1400°F.) 18-8 is resistant to scaling in air and has good creep strength.

2. Above 760°C. (1400°F.) scaling and intergranular oxidation reduce the usefulness of 18-8. The creep strength above 760°C. (1400°F.) is so low that appreciable internal pressure could be allowed only as a semi-experimental procedure.

3. Titanium addition to 18-8 has no appreciable effect on the corrosion resistance or physical properties. It merely stabilizes 18-8 against intergranular attack.

4. Columbium does not appreciably affect the general corrosion resistance, merely stabilizes 18-8 against intergranular attack. Columbium increases the creep strength below 650°C. (1200°F.) and increases the stress-rupture strength. It does not affect the coefficient of expansion or the thermal conductivity within design limits.

5. Molybdenum increases the general corrosion resistance and particularly the resistance to chlorides and sulphides. Molybdenum also markedly increases the resistance to pitting. As an alloying element molybdenum is most useful when its tendency to ferrite and sigma formation has been counteracted by readjusting the Cr-Ni ratio as in 16-13-3. The creep strength at all temperatures, particularly above 1400°F. is increased markedly. Likewise the stress rupture

strength is increased. It has no appreciable effect on the coefficient of expansion or thermal conductivity.

6. Proper design to allow for difference in thermal expansion with temperature is essential. Attention to possible carburization, oxidation, sulphidation, erosion, pressure and temperature fluctuations, stress corrosion, and intergranular corrosion will insure proper application and long life of 18-8 in high temperature service.

APPENDIX

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Effect of Carbon on 18 Cr- 8 Ni Alloys	A
Fe-Cr-Ni Constitution Diagram @ 800°C.	B
Typical Time - Elongation Curve	C
Actual Time - Elongation Curve @ 1000°F.	D
Stress vs. Creep Rate for 18-8 @ 1200°F.	E
Temp. vs Creep Strength for 18-8 and 18-8 Ti	F
Temp. vs Creep Strength for 18-8+Cb	G
Temp. vs Creep Strength for 16-13-3	H
Stress vs Time for Rupture for 18-8	I
Stress to Rupture in 1000 hrs. - 18-8, 18-8+Cb, 16-13-3	J
Stress to Rupture in 100,000 hrs. - 18-8, 18-8+Cb, 16-13-3	K
Endurance Limit of 18-8 vs Temp.	L
Coefficient of Linear Expansion vs Temp. for 18-8	M
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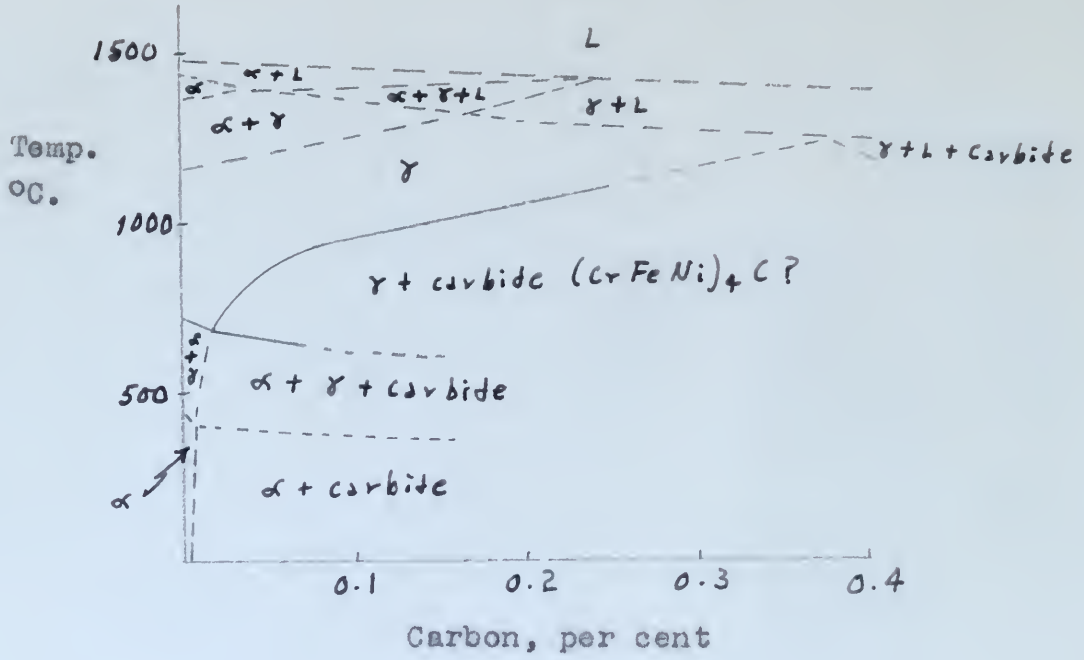
Thermal Conductivity vs Temp. for 18-8	O

The Effect of Carbon on the Constitution of Alloys Containing 18 Per Cent Cr and 8 per Cent Nickel, after Kinzel and Franks.[28]



Note: The dotted lines represent considerable uncertainties.

NO. 340-TC DIETZGEN GRAPH PAPER
TRIANGULAR CO-ORDINATE

EUGENE DIETZGEN CO.
MADE IN U. S. A.

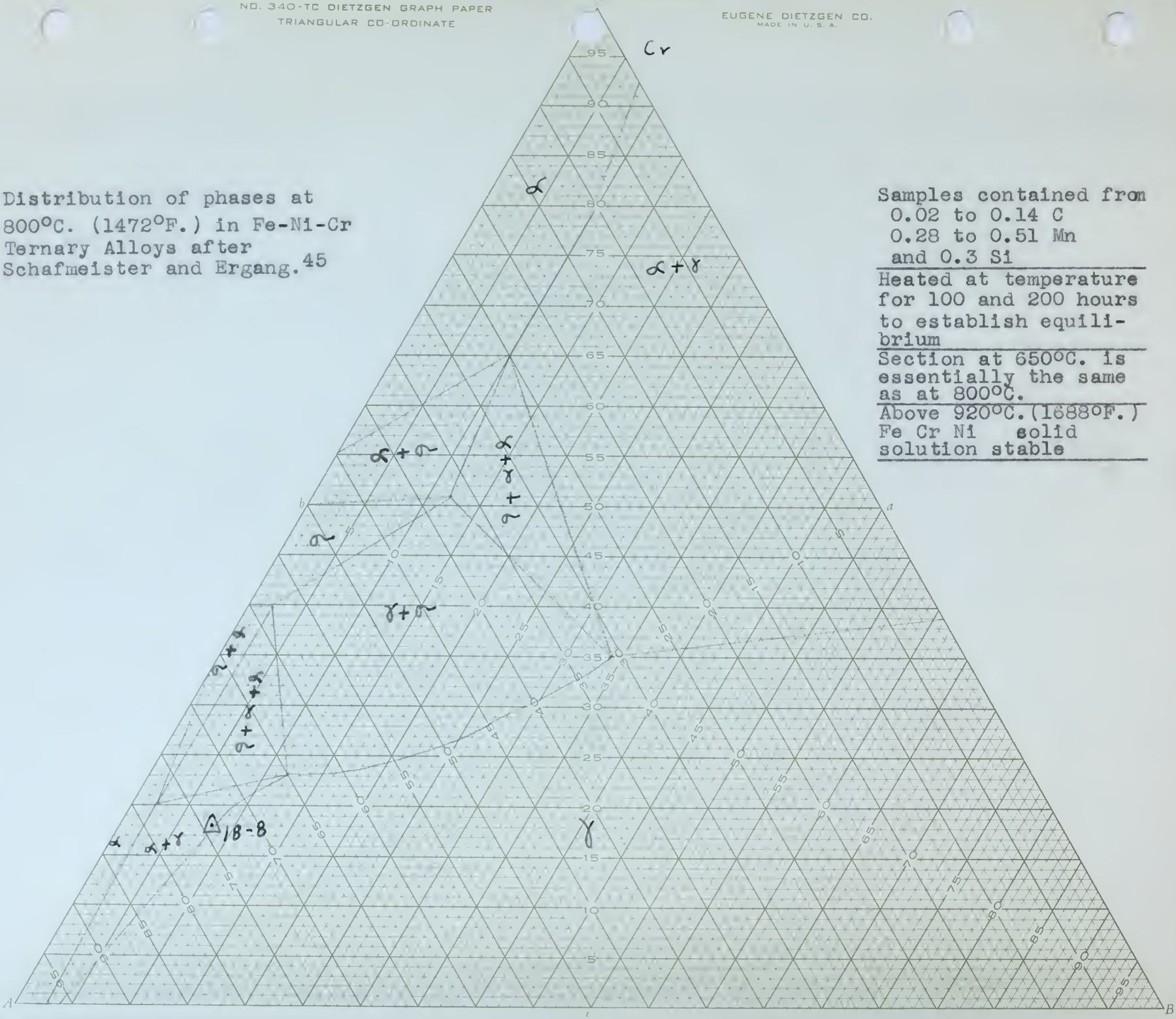
Distribution of phases at 800°C. (1472°F.) in Fe-Ni-Cr Ternary Alloys after Schafmeister and Ergang.[45]

Samples contained from
0.02 to 0.14 C
0.28 to 0.51 Mn
and 0.3 Si

Heated at temperature for 100 and 200 hours to establish equilibrium

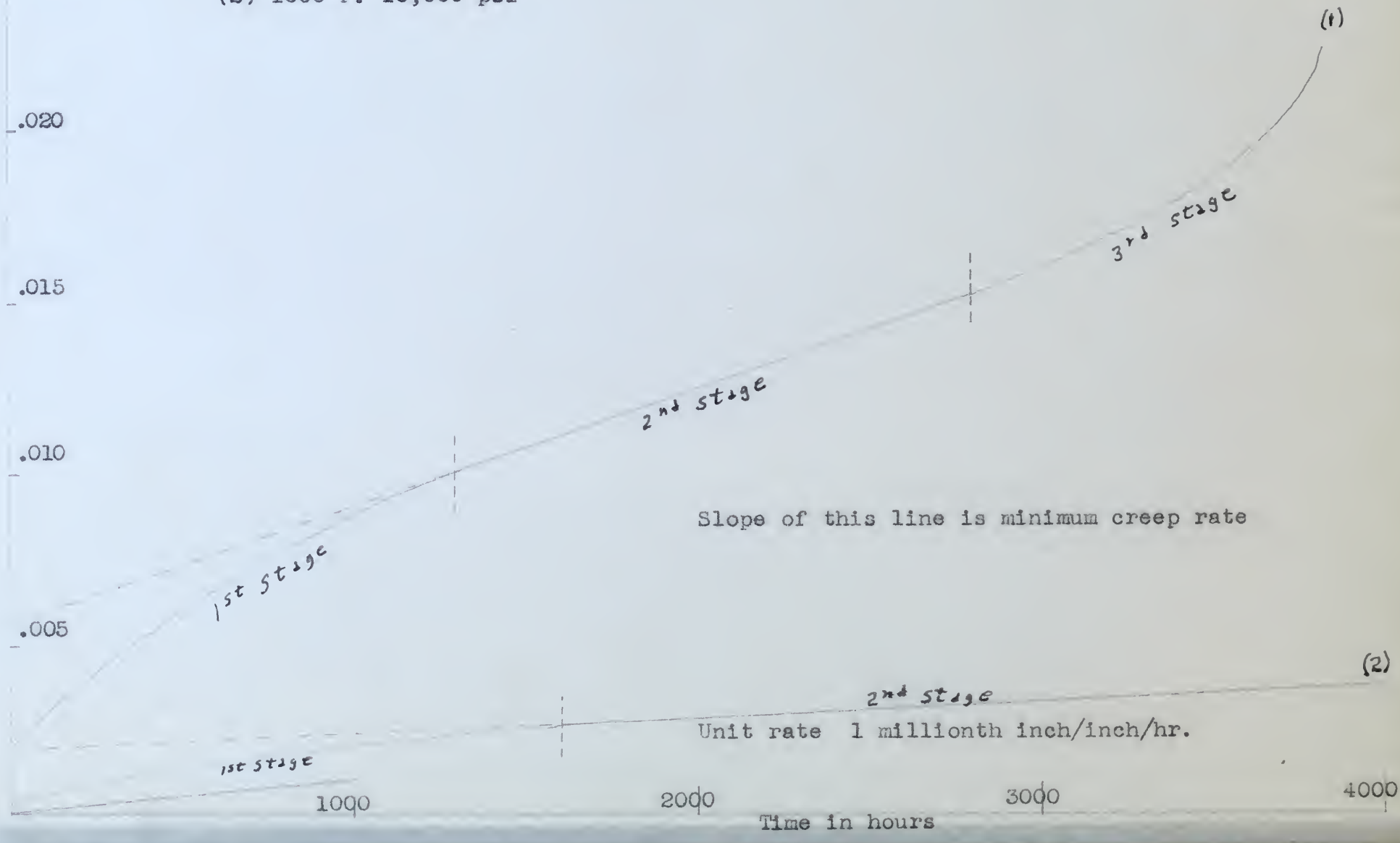
Section at 650°C. is essentially the same as at 800°C.

Above 920°C. (1688°F.) Fe Cr Ni solid solution stable



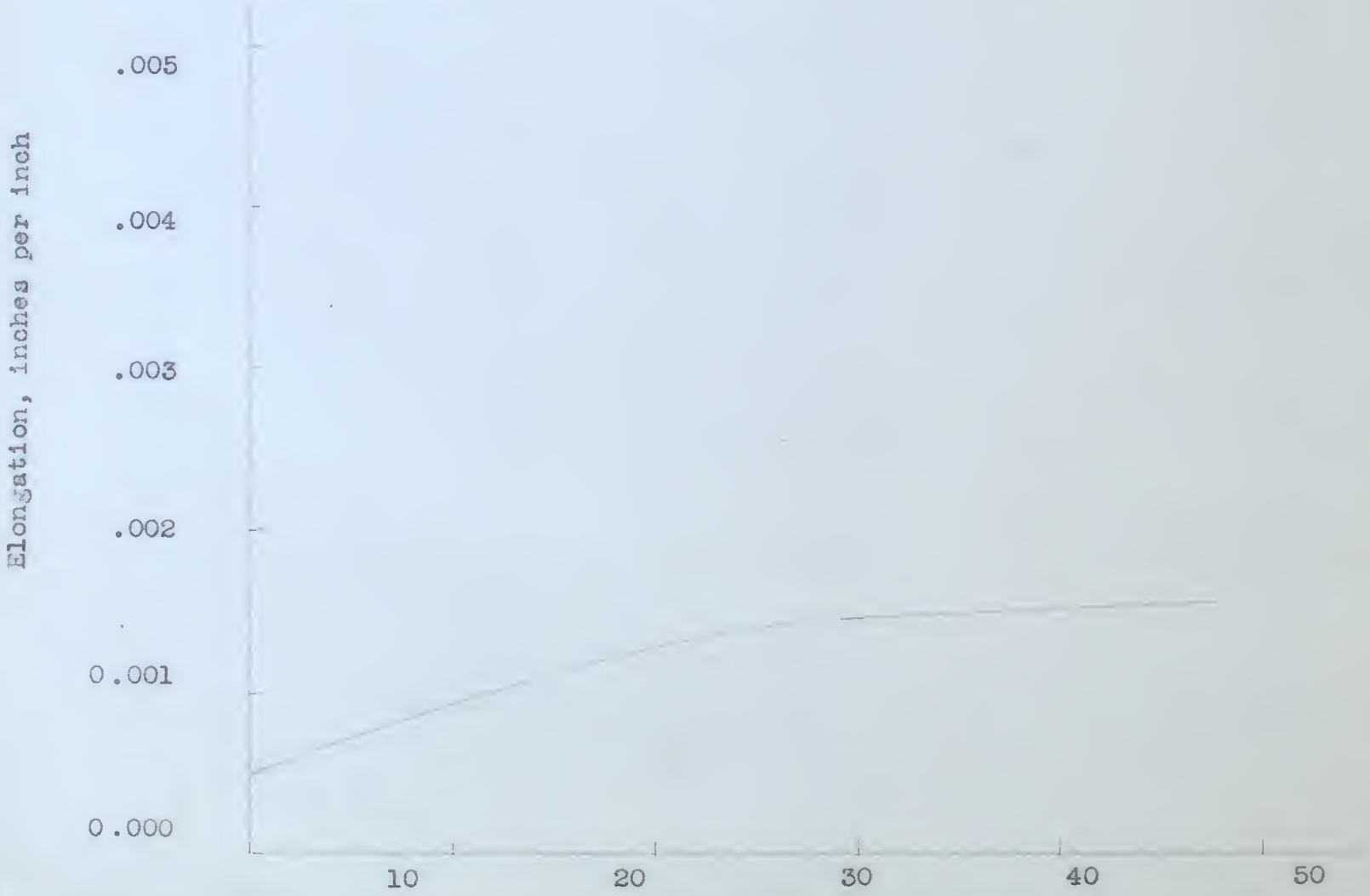
Typical Time - Elongation Curve

(1) 1000°F. 15,000 psi
(2) 1000°F. 10,000 psi



Time - Elongation Curve[57]

Temp. 1000°F.
Load 10,000 psi



Creep Characteristics of Wrought 18 Cr- 8 Ni Steels at 1200°F. (650°C.)[55]

Creep Characteristics of
Tungsten Le Cre- 3 Ni Alloys at
1800°F. (980°C.)

10%

1%

0.01

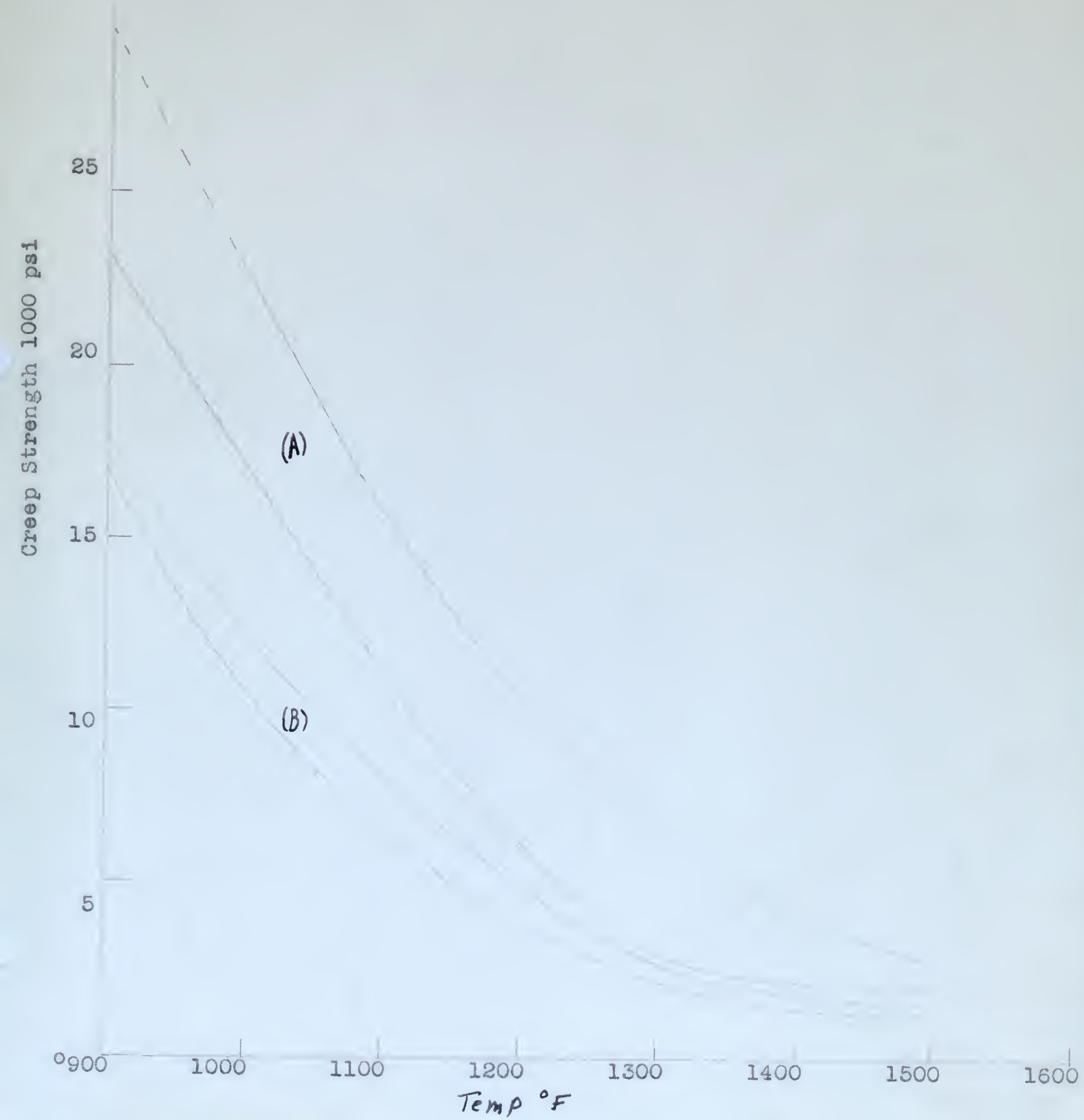
0.1

1

Time at Creep - 5 per 1000 hrs.

Temp. vs. Creep Strength
for
18 Cr-8 Ni Steel[11,55,56,57,58]
(304)*

Curve A - Secondary Creep Rate of 0.10% in 1000 hrs.
Curve B - Secondary Creep Rate of 0.01% in 1000 hrs.
*18 Cr -8 Ni + Ti (321) is similar.

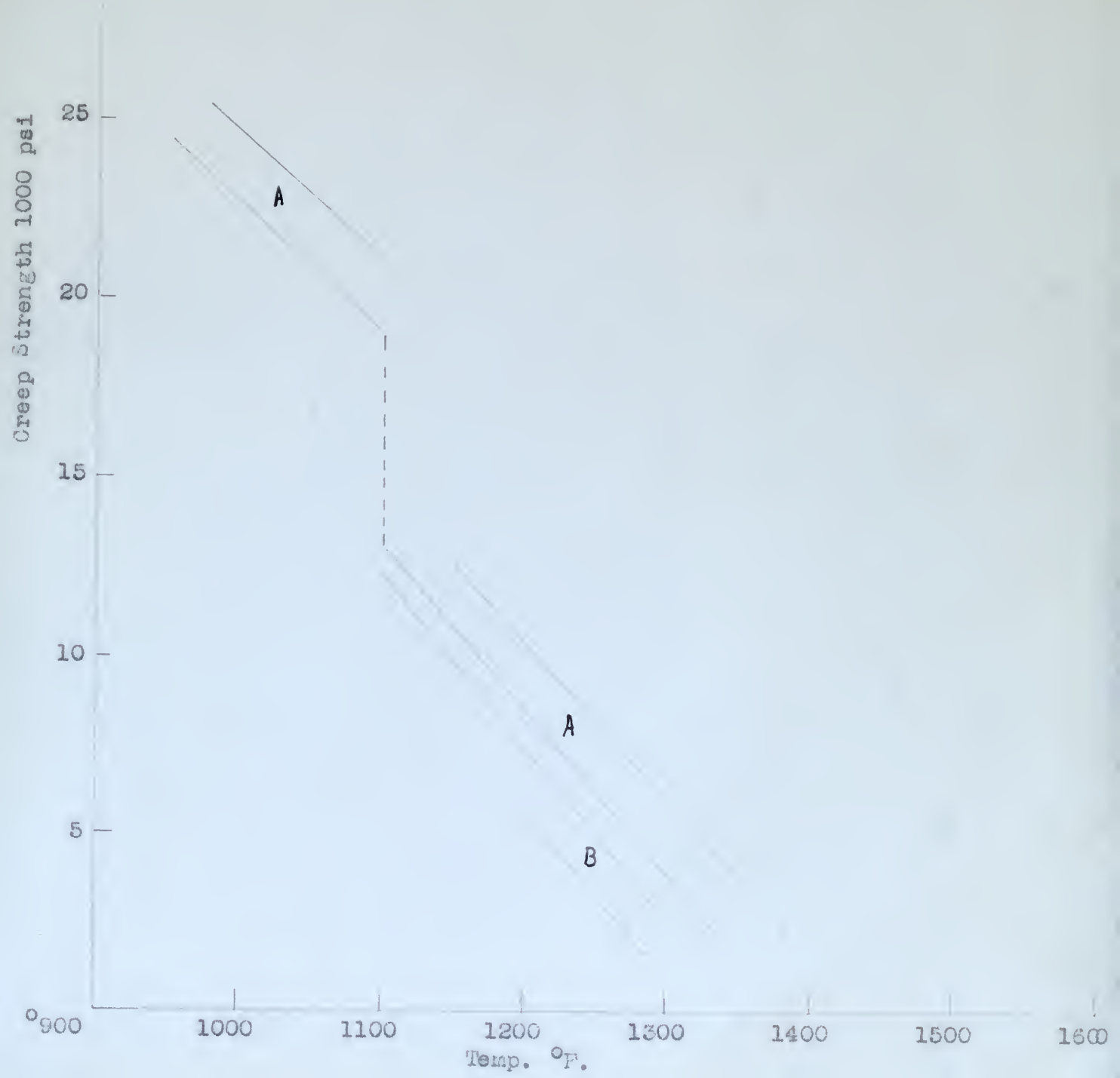


Log (Log 1/Creep rate) (sec)
(A)
(B)

Temp. vs. Creep Strength
for
18 Cr- 8 Ni + Cb Steel[11,57]
(347)

Curve A - Secondary Creep Rate of 0.10% in 1000 hrs.

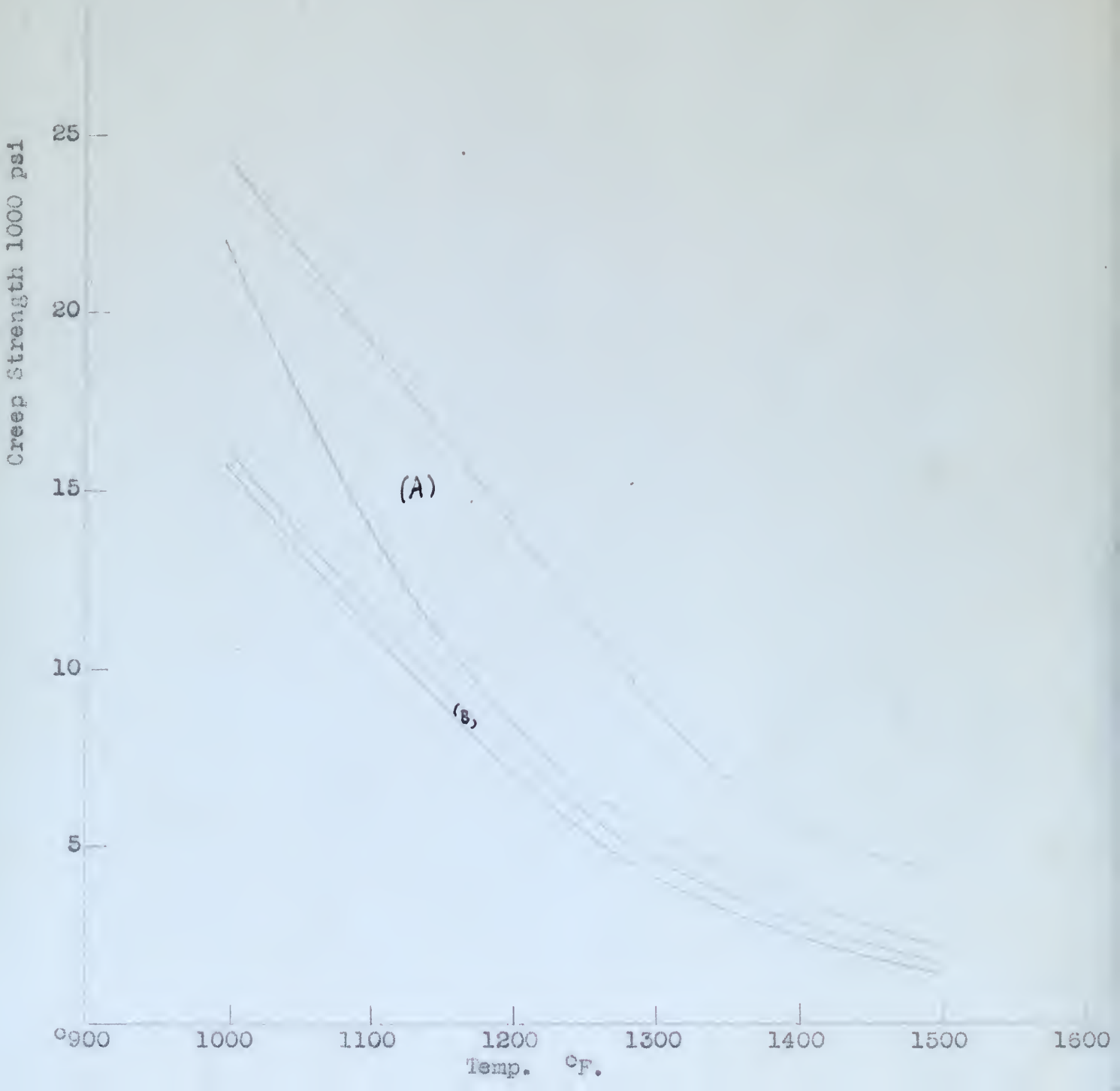
Curve B - Secondary Creep Rate of 0.01% in 1000 hrs.



A
B

Temp. vs. Creep Strength
for
16 Cr- 13 Ni- 3 Mo Steel[11,56,57]
(316)

Curve A - Secondary Creep Rate of 0.10% in 1000 hrs.
Curve B - Secondary Creep Rate of 0.01% in 1000 hrs.



(A)

Stress vs Time for Rupture of 18-8 1500°F. after White, Clark & Wilson[illegible]

Stress, 1000 psi

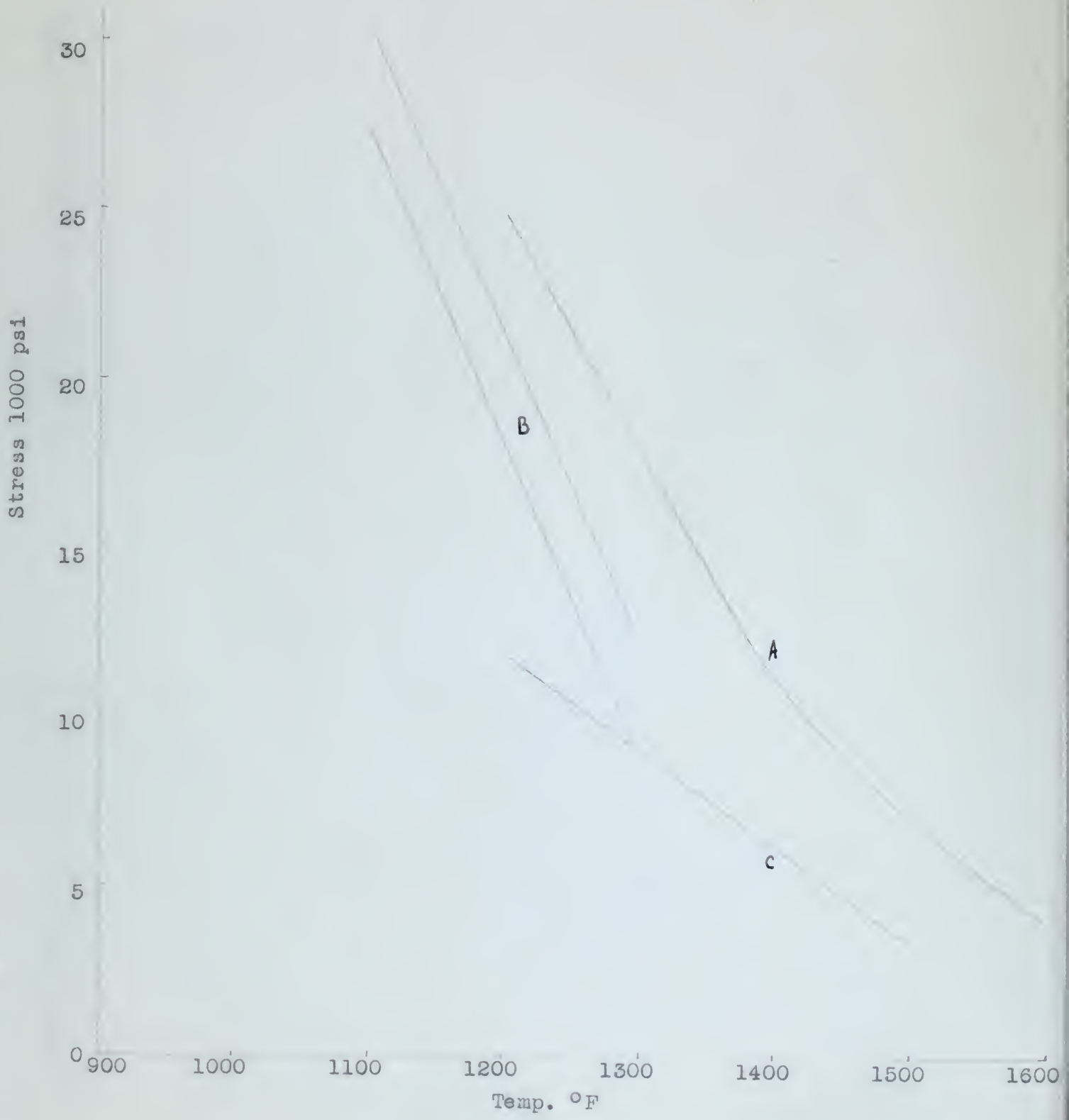
Time for Rupture, Hours

Intergranular oxidation believed to have occurred here.

KEUFFEL & ESSER CO., N.Y. NO. 359-125LG
Logarithmic, 5 x 3 Cycles
MADE IN U.S.A.

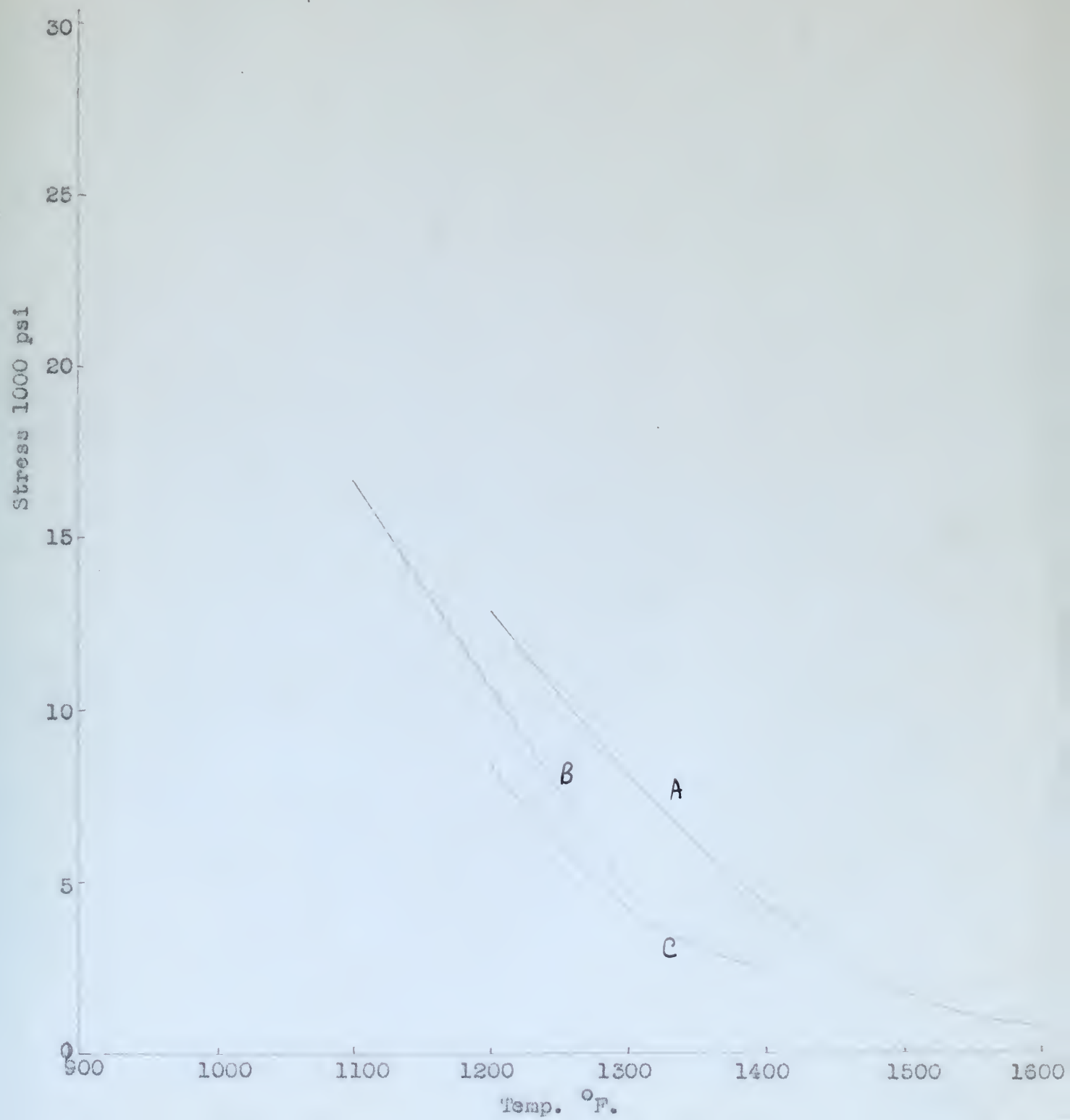
Stress - to - Rupture
in 1000 hrs.[11,53,56,57]

Curve A - 16 Cr-13 Ni-3 Mo Steel (316)
Curve B - 18 Cr-8 Ni - Cb Steel (347)
Curve C - 18 Cr-8 Ni Steel (304)



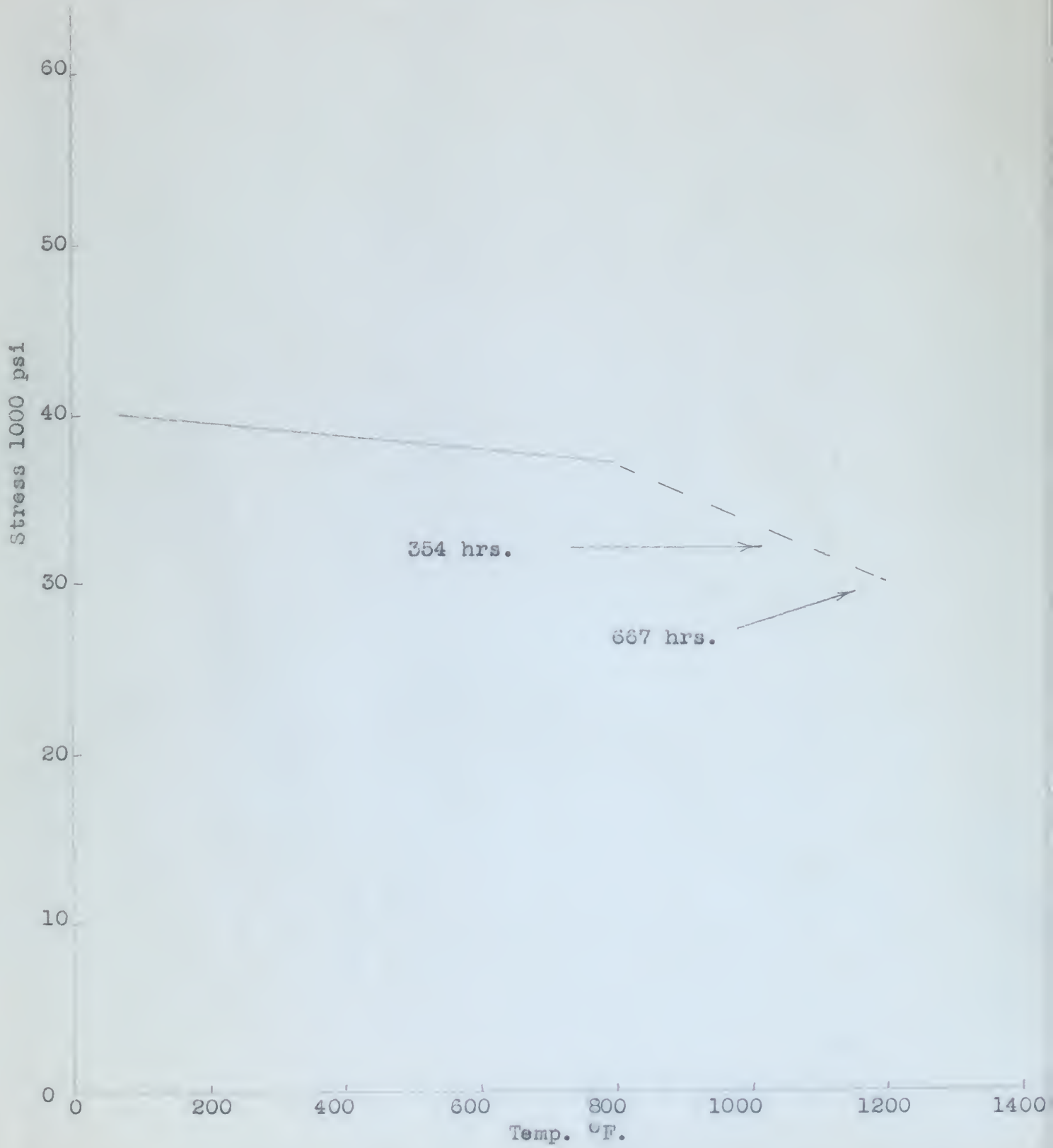
Stress - to - Rupture in 100,000 hrs.[11,55,56] (Extrapolated)

Curve A - 16 Cr-13 Ni-3 Mo Steel (316)
Curve B - 18 Cr-8 Ni- Cb Steel (347)
Curve C - 18 Cr-8 Ni Steel (304)



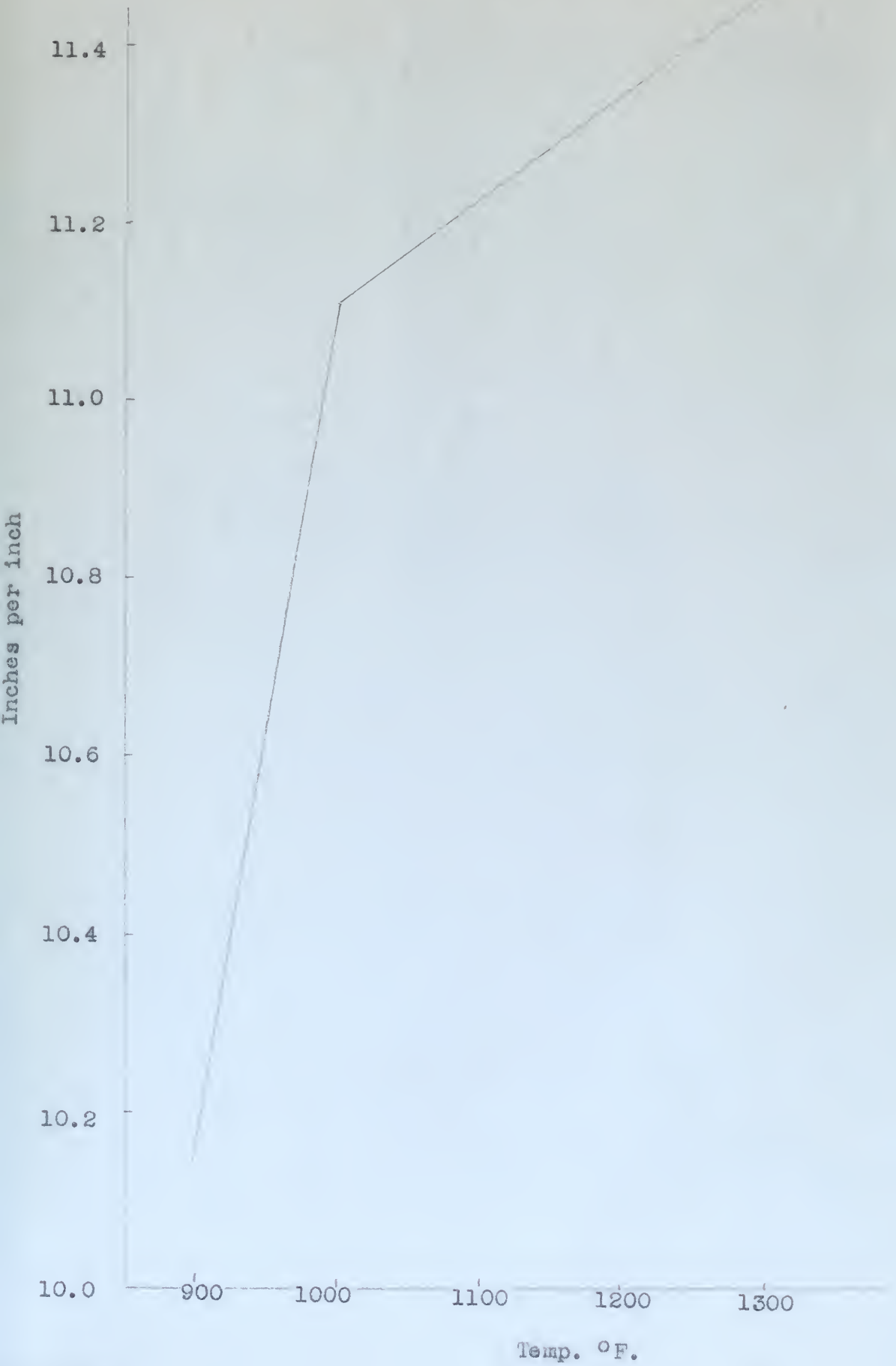
Endurance Limit vs. Temp.
for
18-8 (304)[11]

Above 800°F., no real endurance limit found. Curve represents the trend of the data only.



11.6

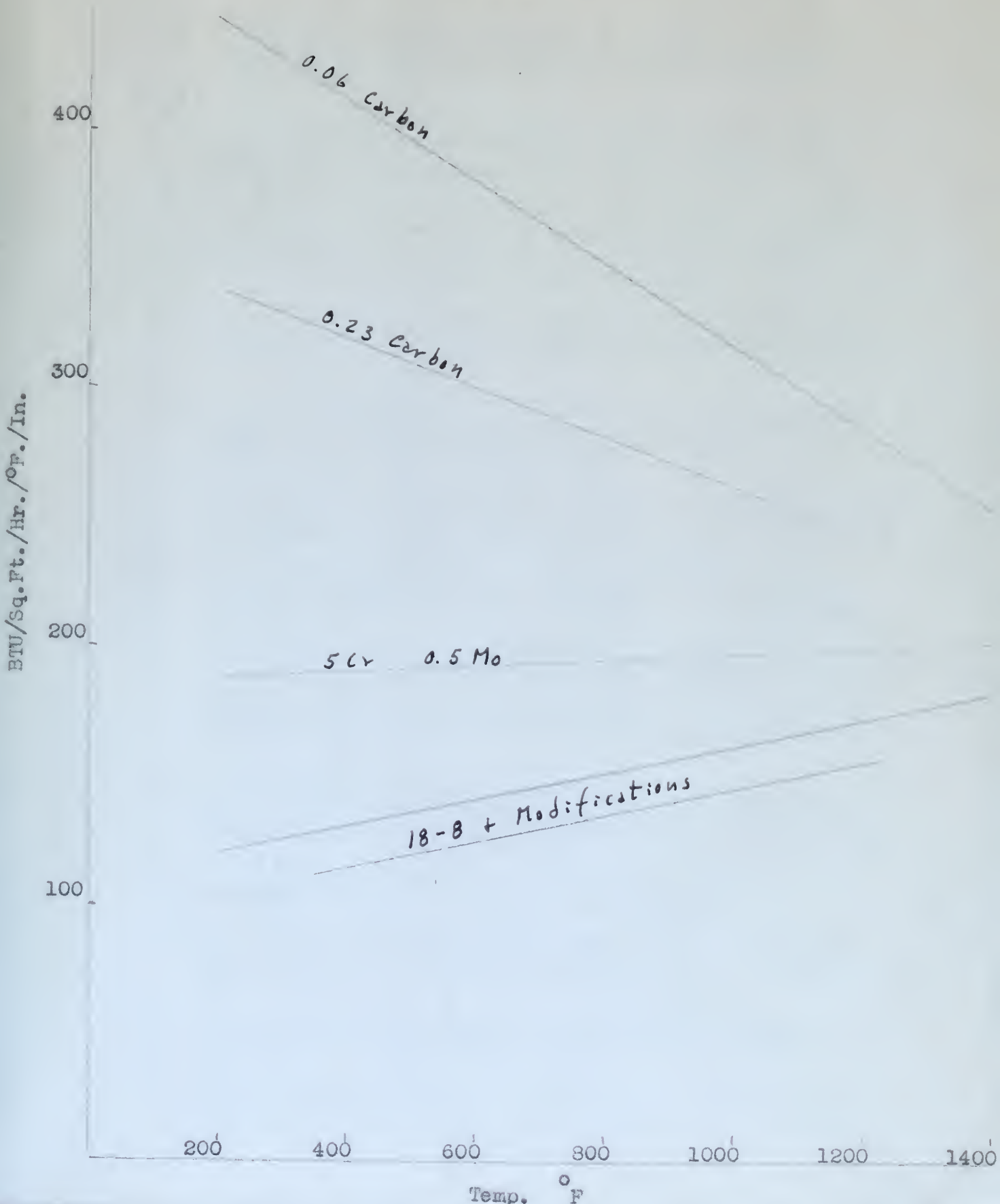
Coefficient of Linear Expansion vs. Temp.[57]
(Inches per inch per $^{o}F.$ x 10^{-6})
18 Cr-8 Ni (304)



Average Coefficient of Linear Expansion
(inches per inch per ^{o}F. x 10^{-6})[56,57]

Temp. Range	18-8		18-8+Cb	16-13-3
	Timken	B & W	Timken	Timken
70 - 900^{o}F.	10.30		9.91	9.98
70 - 1000^{o}F.	10.38	10.20	10.02	10.07
70 - 1100^{o}F.	10.49		10.16	10.16
70 - 1200^{o}F.	10.65	10.41	10.30	10.29
70 - 1300^{o}F.	10.75	10.50	10.39	10.37

Thermal Conductivity of Various Metals[11,56,57]



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